COMMONWEALTH BUREAU OF SOIL SCIENCE

TECHNICAL COMMUNICATION No. 44

THE SPECTROGRAPHIC ANALYSIS OF SOILS, PLANTS AND RELATED MATERIALS

by

R. L. MITCHELL

(Macaulay Institute for Soil Research, Aberdeen)

Price, 12*s*. 6*d*.

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PREFACE

This Technical Communication is an attempt to review the literature on spectrographic methods of analysis that are relevant to the investigation of soils, plants and related substances such as soil parent materials, fertilizers and animal products, and to present some details of the methods of analysis which have been worked out over the past 12 years in the Spectrographic Department of the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen.

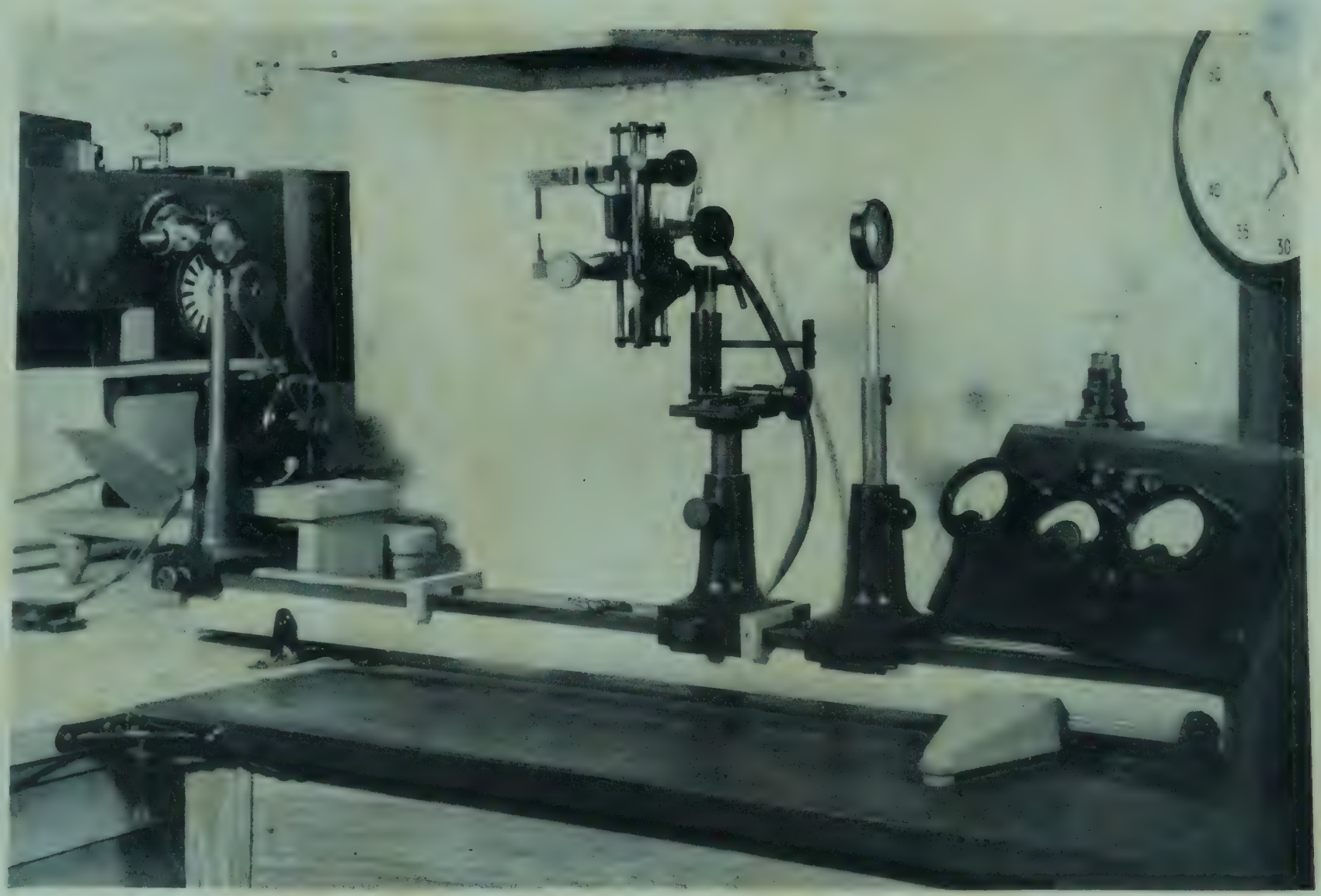
The Author makes grateful acknowledgement of the valuable assistance of the members of the staff of the Spectrographic Department and in particular to Dr. R. O. Scott who has been responsible for the spectrum photograph in Appendix III and for a spectrographic card index bibliography of some 4,000 entries, without which the preparation of this communication would have been impossible in the time available. The spectrographic work has been carried out with the assistance of grants from the Agricultural Research Council for the purchase of equipment.

Throughout the text, some inconsistencies in wavelengths of spectral lines may be noticed. This is generally due to the fact that the actual values given by the authors are quoted. Otherwise, the values from Harrison's Wavelength Tables, rounded off to 4, 5 or 6 figures, have been employed.

The order of presentation of the chapters is that which has, on consideration, appeared to involve the most straightforward description, despite the apparent inconsistency of discussing the photographic plate and photometry before the various spectral sources.

CRAIGIEBUCKLER,
ABERDEEN

R. L. MITCHELL



Spectrographic equipment for the determination of trace constituents in soils and plant materials

THE SPECTROGRAPHIC ANALYSIS OF SOILS, PLANTS AND RELATED MATERIALS

Chapter 1

INTRODUCTION

The spectrograph is an instrument for the analysis of radiation. In the form employed in practical analytical work for the examination of the radiation from flames and electric discharges, the dispersing agent is a quartz prism or a diffracting grating ; the wavelength range covered can be taken as approximately 2000-10,000 Ångstrom Units (A) where A = 10^{-8} cm.

When an atom of any element is energized, either thermally or electrically, radiation is emitted as it returns to its initial or ground state, and those elements which emit radiation within the above wavelength range can be detected and determined by the methods of spectrographic analysis. The mechanism of the emission will be considered further in the next chapter: the process depends on the fact that the bulk of the emission from any element appears as radiation of one or more characteristic wavelengths, and not as continuous radiation over a wide range of wavelengths, as is obtained in black body radiation. The individual wavelengths are characteristic of the atom of the element producing them and provide a clue to its identity, as coincidences are not frequent. This radiation is passed either directly or by means of a lens or mirror into the narrow entrance slit of a spectrograph. In the prism spectrograph the radiation which has entered the slit is made parallel by means of a collimating lens and then dispersed by a 60° quartz prism which, because of the variation of refractive index with wavelength, turns light of different wavelengths through different angles. Thereafter a camera lens brings the radiations to a focus on a photographic plate, which in effect reproduces a series of monochromatic images of the slit, one for each constituent wavelength of the radiation entering the slit. The position of the image on the plate is determined by the wavelength of the light causing it, whilst its density is dependent, amongst other factors, on the intensity of the radiation of that wavelength.

The light (used as a general term to include the infra-red and ultra-violet radiations in the 2000-10,000A range as well as visible light in the

4000-8000A range) emitted from any source can thus be split up into its constituent wavelengths, or spectral lines. Quartz optical equipment is necessary in order to include the ultra-violet spectrum below 3500A, at which wavelength most glasses begin to absorb. The practical lower limit at 2000-2200A results from absorption by air and the gelatine of the emulsion. The theory and design of spectrographs is dealt with by Kayser (1900), Baly (1924, 1927 a, b) and Sawyer (1944).

In recent years, particularly during the past ten to fifteen years, the use of spectrographic methods for the analysis of all types of materials, from metals and alloys to biological tissues, has extended rapidly. It is intended in this Technical Communication to indicate such of these developments as are applicable to the analysis of soils and plant materials, as well as of materials such as rocks and minerals, fertilizers, waters and animal tissues with which soils and plants are fundamentally interrelated. The materials involved in this work are mainly solutions and non-conducting powders, so that the relevant spectrographic methods are those which deal with such materials, although, from the purely spectrographic aspect, important developments and contributions made in papers dealing with the analysis of apparently unrelated materials such as metals and alloys have been considered where they are capable of wider application.

In view of the probable adoption of the spectrograph by many non-specialist laboratories as a routine tool, it has seemed desirable to include a short summary of the principles on which spectrographic analysis is based and of the types of equipment available. For a fuller discussion of the general principles of spectrographic analysis reference should be made to the monographs of Scheibe (1933), Twyman (1941), Brode (1943) and Sawyer (1944) and to such shorter accounts as those of Lewis (1936), Swings (1935), Bureau (1938), Henrici and Scheibe (1939) or Gerlach and Schweitzer (1930 a). Earlier accounts, such as that of Urbain (1911), are of interest from the historical aspect. The very scattered literature on spectrographic analysis and its applications has been covered to some extent by bibliographies and collections of abstracts by Scheibe (1933), Twyman (1938), Henrici and Scheibe (1939), Smith (1940), Someren (1941, 1947), Meggers and Scribner (1941), Hodge (1946) and Scribner and Meggers (1947), but all of these are incomplete. Kayser (1900) gives many references to early work. Amongst current periodicals containing material of spectrographic interest are *Journal of the Society of Chemical Industry*, *Journal of the Optical Society of America*, *Industrial and Engineering Chemistry* (*analytical edition*), now appearing under its new name *Analytical Chemistry*,and *Spectrochimica Acta*, now being published from Vatican City. All should be accessible to every spectrographic laboratory.

Diffraction gratings suitable for spectrographic analysis have recently become available in the United States and much work is being done with grating spectrographs, particularly in metallurgical work. These instruments have the advantage of a nearly linear wavelength dispersion,

whilst a prism instrument gives a much greater dispersion at the short wavelength end of the spectrum than in the red, the dispersion being roughly defined as the distance apart on the plate of lines of a given wavelength difference. On the other hand, a grating gives spectra of several orders at the same time, and lines of higher orders may overlap those of the first order. In a good grating a considerable proportion of the light can be put into the first order. The relative merits of the two types of spectrographs are discussed by Harrison (1938), Slavin (1940 a), Twyman (1941) and Sawyer (1944) : the author has no personal experience of grating instruments. These have seldom been used in biological work, although Nelson (1942) has described a suitable design.

The dispersion of a spectrograph is the chief factor in the choice of a suitable instrument. It is in general not the elements to be determined, but the source to be used and the composition of the material to be examined, in so far as its major constituents are concerned, which decide the instrument to be used. With a flame source, for instance, even such elements as iron or manganese which are relatively rich in lines show only a few of the more easily excited lines, and a spectrograph of moderate dispersion, such as the Hilger Medium or Intermediate Quartz spectrograph, is adequate. In an arc or spark source, on the other hand, where even a few per cent of iron may produce several thousand lines, a large dispersion is often required to separate adequately the iron lines from those of other elements which have to be determined. The spectrograph most convenient for the determination of such trace constituents as cobalt, gallium or lead in an iron rich material is the Littrow design typified by the Hilger Large Quartz spectrograph. A Littrow spectrograph is unlike the smaller types in that, to effect economy in size, a half prism with a mirror is used, the light being reflected back to a plate holder adjoining the slit. Ability to resolve lines 0.2A apart at 3500A so that photometric measurements can be made on each, can be taken as criterion of suitability of a spectrograph for such determinations.

The dispersion given by a glass prism is about 3 times that of quartz, so, for the wavelength regions for which it is transparent, it has certain advantages, particularly when dealing with such elements as the alkalis, alkaline earths and rare earths, whose most sensitive spectral lines are in the visible region. Certain of the Littrow instruments can be obtained with an interchangeable glass train in addition to quartz, whilst there are several suitable glass spectrographs by Hilger and Zeiss in addition to those described by Mannkopff (1931) and Tongeren (1938). There is a tendency for modern American instruments to use film rather than plate to record the spectrogram, but such equipment is not generally available in Britain, and it is doubtful if any advantage is gained by the use of film.

There are three main steps in the determination of any element by emission spectrography. The material being examined must be raised to a sufficiently high temperature, or otherwise energized, so that the radiations characteristic of the constituent atoms or ions are emitted. This light is

then split up into its constituent wavelengths and recorded as a spectrogram on the photographic plate or film of a prism or grating spectrograph. Finally the densities of the recorded spectral lines are measured by means of a microphotometer or densitometer, and the actual content of the element ascertained by comparison with a calibration curve derived from known samples, or by some similar method. The process depends on the fact that, under precisely standardized conditions, the intensity of the spectral line of an element is a function of the amount of the element producing the emission.

The classical methods of excitation are the flame, the electric arc and the high voltage electric spark, but of late the realization of the precise conditions prevailing in arc and spark discharges has led to the distinction becoming less hard and fast, with types of discharges intermediate in nature, or combining the two, being employed. Combined spark-flame sources are also occasionally employed. The practical problem, especially with liquids and non-conducting powders, is to introduce the sample into the source in a reproducible manner. In the flame, liquids can be introduced as a fine spray in the air supply, or on a solid support such as filter paper, whilst for arc and spark sources the normal practice is to carry the powder or evaporated liquid on a conducting electrode which is free from the elements being determined. Carbon, graphite, copper or silver are the materials which are generally employed as electrodes.

Of the ninety-two elements, some seventy, including Ag, Al, As, Au, B, Ba, Be, Bi, C, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Ra, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, can be detected by the normal methods of spectrographic analysis. Certain elements such as Ce, Ta, Te are rather insensitive and may not be detected if present in small quantity in complex mixtures, whilst F depends on the presence of Ca for the production of the sensitive CaF band. A few other non-metals can be excited by special techniques such as those of Fenner (1939) and Feldman (1945) for Se, Blank and Sventitski (1944) for S, or Pfeilsticker (1940) for many non-metals. It is doubtful if such border line elements should be included in the above list. They are not observed by the standard techniques and have to be sought by specific methods before their presence is detected. The usefulness of spectrographic analysis in providing a simultaneous detection of several elements is absent as far as they are concerned.

The choice of the source employed depends on the elements in which the worker is interested and on the concentrations in which they are present. The most sensitive source is some form of arc, and only in this can all the above list be observed. In the flame, on the other hand, only about half of the above elements can be detected, Lundegårdh (1934) reporting, for the air-acetylene flame, suitable wavelengths for 34 elements, namely, Ag, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, Hg, In, K, La,

Li, Mg, Mn, Na, Nd, Ni, Pb, Pd, Pr, Rb, Rh, Ru, Sc, Sr, Tl, Y, Zn, whilst Waibel (1935) determined Ra, omitted from Lundegårdh's list. A few of these quoted, such as Cd, Hg and Zn, are quite insensitive and generally require arc or spark excitation. Even if an element be energized in the flame, the sensitivity is usually considerably less than that obtainable in the arc, and for trace element work the latter is the more useful source. The usefulness of the spark is so limited that consideration of it can be omitted at this point.

Spectrographic analysis provides a method for the estimation of certain constituents in soils and plants. It is often associated specifically with the determination of trace constituents, but so far its most widespread application in agricultural work has probably been the determination of alkali and alkaline earth metals in solution by a flame method. Such determinations can be carried out on a routine scale with an accuracy at least as good as that given by the chemical methods normally employed. The chief applications have been to the determination of the easily soluble or exchangeable soil constituents or to extracts of plant materials. Spectrographic analysis, it must be pointed out, does not provide a method of soil analysis whereby all availability problems can be circumvented, and this applies just as much to trace element determinations, which are now being obtained for many elements for the first time as a result of the application of spectrographic methods, as it does to determinations of the more usually determined constituents. Until adequate information has been amassed on the normal contents of soils, soil extracts and plant materials, and on the amounts necessary for the healthy growth of plants and of the animals feeding on them, the interpretation of the results of spectrographic analyses will probably remain a more difficult problem than the actual analytical determinations.

The possible lines of application of spectrographic methods to agricultural problems have been discussed by several authors, including Ballard (1940 a, c) and Rogers (1941). A recent survey of the methods in use at the Macaulay Institute has been given by Mitchell (1946). A short general review of previous work is that of Mitchell (1947). A paragraph from Ballard (1940 a) is well worth quoting because of the existence of popular misconception on the point covered.

" It should be noted that extravagant (or perhaps, more correctly, overenthusiastic) claims have been made for the spectrograph as an analytical tool by some spectroscopists and by manufacturers of spectroscopic equipment. It must be stated that the spectrograph is not the panacea for all analytical ills. In the opinion of the writer the spectrograph is a very powerful analytical tool, but is most effective when used not individually, but rather in conjunction with the standard bench methods. Some types of analysis can be carried out more easily and accurately by chemical methods, others by the spectrograph. Therefore it is desirable that the analyst should appreciate the particular advantages of each of these two technics."

There are several descriptions of spectrographic laboratory lay-out which may be of use, such as those of Vincent, Sawyer and Sampson (1938), Wilson (1940) or Twyman (1941), but these can in general only be considered to be indications of the type of accommodation required. It is difficult to give detailed recommendations for the lay-out of a complete spectrographic unit for agricultural purposes. It would comprise a chemical laboratory suitable for microchemical work, a room for electrode preparation, with which might be combined a balance room, two spectrograph rooms (one medium and one large spectrograph) with appropriate dark room facilities, a microphotometer room and an office with adequate bench or desk space for calculations. The preference of the author is for a suite of small rooms rather than the use of larger laboratories for several purposes.

Chapter 2

THE EMISSION OF SPECTRAL LINES

Emission spectrographic analysis makes use of the radiation emitted by a neutral or ionized atom which, having been previously energized in some manner, is returning to its normal or ground state. Energization raises one or more of the outer valency electrons of the atom into an orbit, or quantized energy level, further from the nucleus, and the return of the electron to its normal position of lower energy content is accompanied by the emission of energy in the form of radiation of a wavelength equivalent to the amount of energy involved. The emission does not necessarily occur as radiation of a single wavelength. The electron may pass back in a series of steps corresponding to intermediate orbits, the return to the ground state being accompanied by the emission of several spectral lines. The greater the number of electrons and levels involved, the more complex is the spectrum. The wavelengths of the lines are dependent on the energy differences between the steps. The energy E involved may be represented by the difference in energy of the two electronic states of energies E_2 and E_1

$$E = E_2 - E_1 = h\nu$$

when h is Planck's constant and ν the frequency of the light emitted. The relationship between frequency, wavelength λ, wave number ν' and speed of light c is given by

$$\frac{1}{\lambda} = \nu' = \frac{\nu}{c}$$

The energy levels associated with the various electronic states are known as Terms, and the Rydberg-Ritz combination principle was the initial statement of the above energy equation, stating that the wavelengths or frequencies of all spectral lines of an element could be arranged in series and expressed as the difference of two terms

$$\nu' = \frac{R}{x^2} - \frac{R}{y^2}$$

one of which was constant for any series whilst the other varied. For all but the simplest atoms four such series can generally be distinguished, namely, Principal, Sharp, Diffuse and Fundamental (or Bergmann). The names sharp and diffuse describe to some extent the character of the spectral lines in the series, but principal and especially fundamental are rather misleading names which are retained because their initial letters are employed to distinguish the series.

In each series the frequencies of the lines can be represented as the difference of a constant term (the series term) and a variable term (the current term), thus, writing the above equation in a different form,

$$\nu' = L - \frac{Rz^2}{(n-\delta)^2}$$

where R is the Rydberg number (109,737 cm^{-1} for atoms of higher atomic weight) and z is the effective charge, being equal to 1 for unionized atoms. n is a whole number, whilst δ is an approximate constant for any series. The value L is the convergence limit for any series, obtained by putting n equal to infinity. A convenient shorthand notation for the different series, implying the above equation, is

Principal series	$\nu' = 1S - nP$	$n = 2, 3, 4 \ldots$
Sharp series	$\nu' = 2P - nS$	$n = 2, 3, 4 \ldots$
Diffuse series	$\nu' = 2P - nD$	$n = 3, 4, 5 \ldots$
Fundamental series	$\nu' = 3D - nF$	$n = 4, 5, 6 \ldots$

Because of restrictions shortly to be mentioned, there are certain combinations which are prohibited, thus we find S combining only with P, P with S or D, and D with P or F, but not, for instance, S with D or F.

n is the principal quantum number of the level in which the electron involved is situated, but its state is not completely defined by this value : certain of the orbits can be considered to be disposed elliptically to the nucleus and to have eccentricities giving azimuthal quantum numbers k of from 1 to n. Wave mechanical considerations bring out one of the difficulties of the orbital model of the atom by showing, in accord with experience, that these values should run not from 1 to n but from 0 to n-1, and, to avoid ambiguity, this azimuthal quantum number, generally known as l, is stated as a suffix to the principal quantum number of the electron by means of a letter thus

l =	0	1	2	3	4	5	. . .
symbol	s	p	d	f	g	h	. . .

The value of l for the electron thus defines the series of the spectral line which it produces. In addition to this angular momentum l, there is a spin moment s of the electron to be considered. s has a value of $\frac{1}{2}$, and contributes to the resultant angular momentum j, which can have values of $l + \frac{1}{2}$ or $l - \frac{1}{2}$, except for $l = 0$, where only $j = \frac{1}{2}$ is possible.

Thus an electron with principal quantum number 4, l value of 2 and j of $1\frac{1}{2}$ would be indicated as $4d_{3/2}$. This symbol refers to the electron and not to the energy level, but the distinction need be made only where more than one electron occupies the level in question. For the description of an electron configuration a symbol such as $2p^3 3s3p$ is used, meaning three electrons $n = 2$, $l = 1$, one electron $n = 3$, $l = 0$ and one electron $n = 3$, $l = 1$. Generally only the outermost electrons are indicated, as the inner groups are not affected by the changes occurring in spectral emission.

Analysis of spectra shows two groups of Terms, odd and even, depending on the sum of the l values of the electrons, and that transitions of electrons can normally occur only between odd and even and not odd to odd or even to even.

Whilst lower case letters are employed to refer to individual electrons, capitals refer to terms, and transitions between terms can only occur for J changes of 0 or ± 1 with the transition $J = 0 \longrightarrow J = 0$ prohibited.

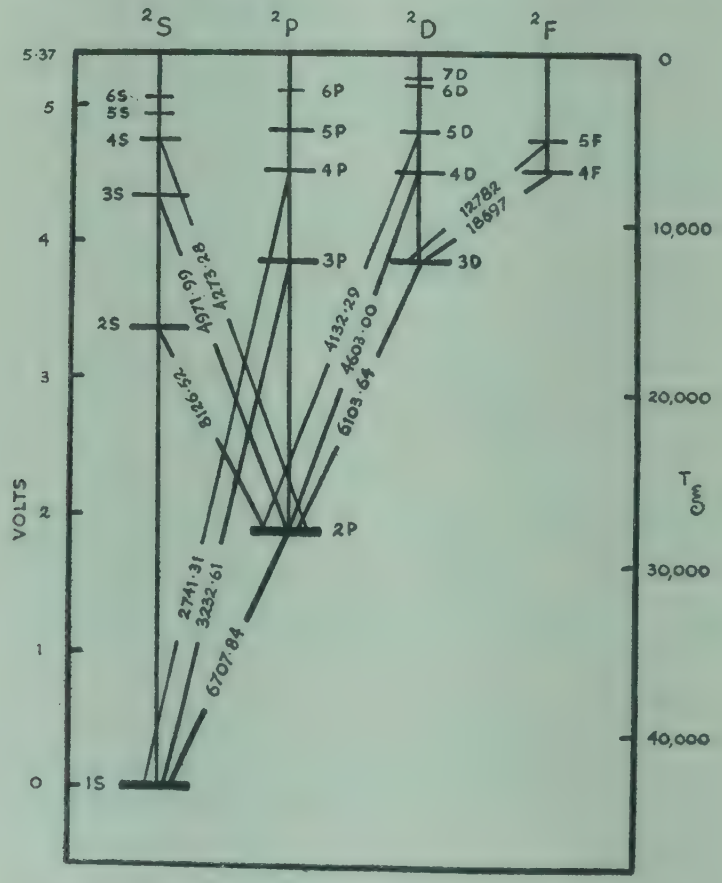


FIG. 1.—Energy level diagram of lithium, after Grotrian (1928)

Thus only certain of the possible electronic transitions are found and these can often, for the simpler atoms with only one or two valency electrons, be demonstrated diagrammatically, following Grotrian (1928). For terms or energy states which can be given definite values of L and S, the same convention is employed for L as for electrons, thus

$$L = 0, 1, 2, 3 \ldots$$
$$\text{symbol} \quad S, P, D, F \ldots$$

whilst the multiplicities denoted by S are :

$S = 0$ singlet	$S = 1\frac{1}{2}$ quartet
$S = \frac{1}{2}$ doublet	$S = 2$ quintet
$S = 1$ triplet	etc.

These arise because for a given S and L there are $2S + 1$ possible J values if $L \geqslant S$. These levels lie together as a multiplet. In the symbols for the terms the multiplicity, i.e. $(2S + 1)$, is added as a superscript at the left hand side of the symbol representing L. Thus ^3D means $S = 1$, $L = 2$ with possible J values 1, 2, 3. The symbols for the three levels are $^3D_1$, $^3D_2$, $^3D_3$.

Fig. 1, after Grotrian, shows the energy level diagram of lithium, with the energy contents of the different levels and the wavelengths of the spectral lines produced by the transitions between the different levels. The strongest line at 6707.8A is shown to be due to a 2P$\longrightarrow$1S transition, and is fully classified as $(2p)^2P_{3/2} \longrightarrow (1s)^2S_{1/2}$.

It is seen that the energy levels approach a maximum corresponding to 5.37 electron volts or 43,500 cm^{-1}, which is the convergence limit L which we have already noted. This is the energy required to remove the electron from the influence of the nucleus completely, in other words to ionize the atom. Hence L is the ionization potential. The ionized atom must be considered as a new system, with a completely different suite of spectral lines caused by transitions of the next most labile electron and giving a spectrum resembling that of the element below it in the periodic system. The spectrum corresponding to the neutral atom of, say, potassium K is called the K I spectrum, whilst ionized K^+ gives the K II spectrum. Rather similar spectra are given by the series K I, Mg II, Al III, Si IV, all of which have a common term system as their electronic structures are similar. The spectrum of the unionized atom is often called the arc spectrum and those of ionized atoms the spark spectra, as they are commonly observed in these sources, but this distinction is not fundamental.

For a fuller discussion of the relationship of atomic structure to spectral emission, reference should be made to such publications as Candler (1937), Herzberg (1937), White (1934), Bacher and Goudsmit (1932) or Glasstone (1940). The above superficial discussion is intended only to define some of the terms required elsewhere in this communication or met in papers on spectrographic analysis. The practical implications of the relationship of the classification of the spectral line to its behaviour as far as spectrographic analysis is concerned are not yet fully established. The choice of suitable

spectral lines for quantitative purposes is, however, no longer quite arbitrary, and it is becoming clear that more definite correlations will eventually be worked out, with a corresponding increase in the accuracy of the results obtainable.

The self-reversal of certain spectral lines is fully explained from our knowledge of atomic structure. The process of energization, resulting in the raising of an electron to a higher energy level, is followed by the loss of a corresponding amount of energy in the form of radiation as the electron falls back to its original position, and this energy is just capable of energizing another atom in the same way. Thus in a source rich in one element which is emitting a considerable amount of energy, some of it is re-absorbed by the atoms of the same element in the cooler gaseous sheath surrounding the hottest part of the source. In the hottest emitting core of the source, the wavelength of the light emitted is somewhat broadened by the Doppler effect, so that a wide line is produced, whilst in the surrounding atmosphere the atoms are cooler and the absorption takes place only over a narrower central wave band. Thus a reversed line appears as a wide bright line with a less bright or even completely dark central strip. In Appendix III it will be seen that most of the strong Fe lines below 2600A in the Fe arc spectrum are reversed. Such lines are clearly not too reliable for quantitative spectrographic analysis and precautions must be taken if they are employed. As self-reversal occurs only with a considerable concentration of the required atom state in the surrounding atmosphere, it can in general occur only with lines which end in the ground state (or a metastable state which can accumulate to an appreciable extent). Hence, if other conditions permit, lines due to transitions ending in the ground state should be avoided in quantitative work.

Meggers (1941 a) points out that the 70 elements searched for in spectrographic analysis are those 70 which have ionization potentials below 10 volts. Ionization potentials have minimum values when the first electron of a given type appears in an atom and maximum values when the shell or sub-shell of this type is complete. Electrons of type p ($l = 1$) are more firmly bound in general than any others, and this makes it difficult to excite the spectra of the noble gases, halogens and metalloids in the presence of elements of low ionization potentials, and often places their strongest lines in the extreme ultra-violet avoided in practical analysis. Meggers points out that whilst the strongest lines do not always involve the normal or ground state of the atom, in every case they are produced by transitions between s and p electrons, and these atoms which possess only one valency s electron (alkalis, Cu, Ag, Au, Cr) exhibit the highest absolute sensitivity. Meggers (1941 b) also deals with the strongest lines of singly ionized atoms, which are typical of spark sources, and points out that the sensitive elements are those with one s electron (Be, Mg, Ca, Zn, Sr, Cd, Ba, Yb) or with one such combined with d or f (21 Sc to 29 Cu ; 39 Y to 47 Ag ; 72 Hf to 79 Au ; 58 Ce to 70 Yb). These give lines of outstanding intensity

and longer wavelengths, those of the ionized rare earths for instance being in the 3500-5000A range.

Knowledge of the classification of any line is useful in quantitative analysis from a further point of view. The general practice at present is to employ an internal standard method in which the intensity of the line to be determined is compared with that of a line of an element present in known amount. For this method to be effective, the lines of the two elements should behave similarly as a result of changes in the source conditions, and quite apart from the effects of the physical properties, particularly volatility, there is some evidence that better results are got by choosing lines due to similar transitions. It is in particular inadvisable to compare a spark line with an arc line if a more reliable pair is available.

The use of iron lines of similar classification as intensity standards has been proposed by Dieke and Crosswhite (1943). The classification of Fe I lines can be obtained from Russell and Moore (1944) whilst Meggers (1946) has given a bibliography of papers on the analysis of atomic spectra, from which the classification of lines of most elements can be traced.

Chapter 3

THE PHOTOGRAPHIC PLATE AND ITS MEASUREMENT

a. The Photographic Plate

The spectrum produced by the spectrograph is recorded as a spectrogram on a photographic plate, and the efficiency of any plate depends on its behaviour towards spectrum lines of different wavelengths and intensity. There are three main properties of a photographic emulsion to be considered when it is used for spectrographic purposes, namely, the wavelength range over which it is sensitive, its speed or sensitivity at different wavelengths and its contrast at these wavelengths.

For the range from about 2200 to 5000A practically any emulsion is sensitive and the choice of a suitable plate depends on the other factors. Above 5000A, up to 10,000A or even further, panchromatic and infra-red sensitizings are available, but here the choice of suitable characteristics is rather more limited. Below 2200A it is often necessary to use special plates, such as Schumann or Ilford Q plates, which reduce gelatine absorption by surface coating of the emulsion, or to sensitize the emulsion by means of some fluorescent substance which produces a secondary image by the emission of light of longer wavelength.

The speed or sensitivity of a photographic emulsion is a factor rather difficult to define as far as suitability for spectrographic purposes is con-

cerned, because no emulsion is uniform in speed over the range of wavelengths to which it is sensitive, whilst no two types of emulsion show the same relative variations. The commercial speeds, determined by the normal methods, are of little value, as they give the response to white light rather than to the monochromatic radiations in which we are interested. In particular they ignore ultra-violet sensitivity, and a so-called slow plate may be faster to ultra-violet radiation than a fast plate.

Probably the most important property in a spectrographic plate is its contrast factor, which is obtained from its characteristic, blackening, or H. and D. curve. This, to be of use for our purpose, must again be for monochromatic radiation of the wavelength in which we are interested. The characteristic curve is the measure of the relationship of the intensity of the incident light to the density of the developed image. The typical shape of a characteristic curve is shown in Fig. 2. The methods of measuring density, and of varying intensity will be considered below. The slope and length of the straight line portion of the characteristic curve is the important property. The maximum slope is the contrast factor, or γ, of the plate for that wavelength, and it is this value which determines the utility of the plate for use over wide or narrow concentration ranges of the elements being estimated, and also to some extent affects the accuracy of the determination. As these factors are antagonistic, the best compromise for the purpose in view must be chosen. Some degree of variation for any particular plate can be obtained by changing the development conditions. The γ of a plate is not constant for different wavelengths but shows a very pronounced increase towards the visible and infra-red region, being lowest and

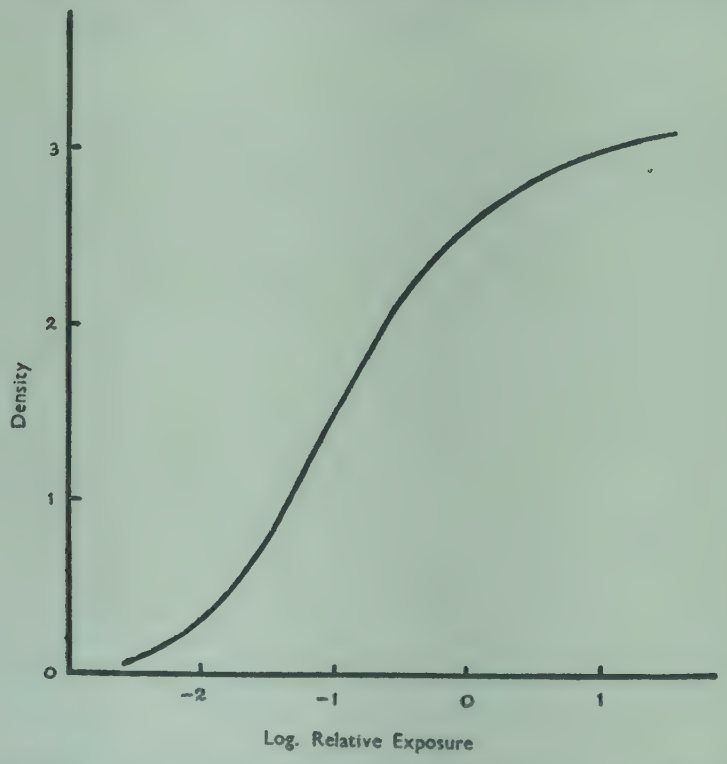


FIG. 2.—A typical characteristic curve of a photographic emulsion

least variable in the ultra-violet. Amstein (1944) and Coates and Amstein (1942 a) have dealt with the relationship of contrast to wavelength and relative speed for a series of the more commonly employed plates, namely Ilford Process, Thin Film Half Tone, Ordinary, Special Rapid, Press, Zenith and Q.I, and Kodak Slow Spectrographic, B5, B10, B20, O120 and P25. Amstein found constant contrast between 2550A and 3050A for all these plates, whilst certain went as low as 2350A or as high as 3250A. At lower wavelengths the contrast fell very steeply except with Q.I, the effect probably being due to absorption by gelatine. The coarser grained plates generally showed a less steep rise of contrast towards higher wavelengths. Similar results have been reported by Pierce and Nachtrieb (1941) for two American emulsions. Davey and Gauntlett (1945) have reported results with the Kodak Uniform Gamma plate, which has a substantially constant contrast up to 4000A. This is achieved by restricting the image to the surface of the emulsion. Unfortunately these plates are rather slow.

Amstein (1944) has given a figure which indicates the relative speeds of the above plates, using the exposure necessary to bring the Co line at 2664A to the start of the useful range of the plate as criterion. For this wavelength, taking Ilford Ordinary as 1.0, the relative speeds varied from 0.78 for Kodak Slow Spectrographic to 7.5 for Ilford Zenith.

By means of special sensitizings it is possible to produce emulsions of different spectral sensitivities and speeds. A series of these has been developed by Kodak, being described in Kodak Data Booklet X37 and in a number of papers by Mees (1931, 1932, 1933, 1935). A useful fast general purpose plate is Ilford Long Range Spectrum which is sensitive from the ultra-violet up to above 8500A. Generally in our work at the Macaulay Institute, Ilford Zenith and Ilford Chromatic plates have been employed, the former for use in flame and the latter in arc work. Chromatic plates were not studied by Amstein but we have found them to be very suitable for trace element work. Above 5000A, Long Range Spectrum plates are used.

The characteristic curve of a plate shows the relationship of the density of the developed image to the exposure which it has received. The density of the image is obtained by measurement, by means of a microphotometer or densitometer, of the light transmitted through the portion of the plate carrying the image, compared with that transmitted by a portion of plate carrying unexposed, developed emulsion. These will be referred to as image and clear plate respectively. The *transmission* of the image is defined as the ratio of the intensity of light (i) transmitted by the image to that transmitted by the clear plate (i_0) ; $T = i/i_0$ or, assuming a linear relationship between the intensity of light being measured and the reading (d) obtained from the microphotometer

$$T = d/d_0$$

The *opacity* is the reciprocal of the transmission

$$O = i_0/i = d_0/d$$

The *density* (which is occasionally referred to as blackening : a term which at least avoids chance of confusion with other types of density measurement in absorption work) is the logarithm of the opacity

$$D = \log (i_0/i) = \log (d_0/d)$$

Unfortunately all these terms have been used very loosely in the literature and it is often difficult to decide what actually is meant. A short list of recommended definitions and symbols has been published by the Spectrographic Discussion Group (Glasgow) (1946).

The processing of spectrographic plates has been considered in some detail by the British Non-Ferrous Metals Research Association Photographic Panel (1945), who found little to choose between rocked-dish and squeegee methods of obtaining uniform development over the plate surface but that brushing was better than either. A developing dish considerably larger than the plate is recommended. Rapid processing of plates is not recommended by the panel and is unlikely to be necessary in biological work to the extent that it is in iron and steel analysis in foundries. If necessary, the methods of Schuch (1942) or Vincent and Sawyer (1939) are capable of producing plates which have been developed, fixed and dried in as little as three minutes.

b. The Microphotometer

In the microphotometer a beam of light from a constant light source is transmitted through the portion of the plate to be measured, and received through the narrow slit of a photoelectric cell. The light reaching the photoelectric cell is measured by means of the effect of the resultant photocurrent on a galvanometer, the response of which should be linear, i.e., directly proportional to the light reaching the photocell slit. The light source should be kept constant over a series of readings but in practice a slow drift is much less objectionable than sudden fluctuations. In the Hilger Microphotometer, a 6 volt 3 amp. bulb is employed and this is conveniently supplied from a 6 volt 120 ampere-hour heavy duty accumulator such as is used in heavy motor vehicles. A simple constant voltage transformer has been found at the Macaulay Institute to be unsuitable, possibly owing to mains fluctuations. Dietert and Hasler (1943) have pointed out that frequency variations lead to considerable irregularities in the output voltage of the usual type of constant voltage transformer and describe an electronic voltage regulator to overcome this effect. Another circuit is given by Parsons (1942). Both supply current at 110 volts. Generally, however, a floating battery circuit should be satisfactory and a simple circuit is suggested by Hilger in the instructions which accompany the Microphotometer. This is given in Fig. 3. The resistance R is adjusted, when the working conditions are established, so that the ammeter A shows no current. The resistance R should be of at least $(V/3 + 10)$ ohms where V is the voltage of the direct current supply available and should be capable of carrying 3 amp. continuously. A more complicated, but probably more efficient, circuit is that of Saunderson and Caldecourt (1944), who reduced

the d.c. voltage in two steps, with an intermediate 18 volt accumulator.

Early types of microphotometers were modified microscopes, incorporating some form of carriage for the plate and having the eyepiece replaced by a photocell. There are many descriptions of such instruments, but for routine spectrographic work it is desirable to have available an instrument specifically designed for the purpose, such as the Hilger Non-recording Photoelectric Microphotometer. The plate is carried on a stage which takes plates up to 6 inches wide and 12 inches long, being easily adjusted for different sizes of plate. The stage can be moved in either horizontal direction to bring any point on the plate into position for measurement. A slow motion drive allows the line to be scanned slowly. This is at present manually operated but provision can be made for a mechanical drive. In order to keep the instrument compact, the light from the 6 volt 18 watt source is reflected at right angles to pass through the plate and again to fall onto the slit of the barrier layer photocell. An objective forms an image of the filament on the plate and another produces a 10 fold image of the plate on the plane of the slit. The area so illuminated on the plate is very small, but introduction of a negative lens into the light path allows a larger area to be inspected for the setting of the plate before measurement. The slit is variable both as regards length and breadth, both being adjusted to a value less than that of the enlarged image of the line being measured.

The photocell response is indicated by the deflexion of the galvanometer. The conventional lamp and scale reading system is now being superseded in all modern designs by some form of projection whereby the reading can be made at a fixed point, past which the scale itself moves. The Hilger Galvoscale unit effects this improvement, which decreases operational fatigue to a great extent, whilst similar devices are built into A.R.L. and Zeiss instruments. It would be advantageous to have a scale with 100 units full scale value in place of the Hilger 50 unit scale, as then densities could be obtained directly by logarithmic plotting. A suitable table for conversion of the values on the 50 basis to densities is, however, available (Mitchell and Scott, 1943 b) and is reprinted here as Appendix I. One disadvantage of the Hilger instrument, especially for less experienced workers who are not able to identify lines at a glance in a small plate region, lies in the selection of the proper line for measurement when a complex spectrogram is being studied. This can be got over by previous spotting of the plate in a comparator, but the practice in certain American instruments of incorporating a projected comparison spectrogram adjoining the slit is convenient. Such instruments are described by Dietert and Schuch (1941) (the A.R.L. Dietert Comparator-Densitometer) and Vincent and Sawyer (1941). A description of the comparable Zeiss instrument (Kerr, 1940) gives details of the galvanometer projection system and of a " tabulating " device enabling the operator to pass quickly from one spectral line to another. The respective merits of different microphotometer designs have been discussed in various publications, such as those of Sawyer (1944) and Churchill (1944).

In quantitative spectrographic analysis of emission spectrograms there seems little advantage in the use of a recording microphotometer which gives a continuous record of intensity changes over a range of wavelengths, rather than a value for a definite wavelength which the non-recording instrument provides. The number of spectrograms which can be read with a recording instrument is considerably less than a non-recording instrument can cover in a similar period. The use of this type of instrument is illustrated by Strock (1936 a) : a modern design with an ink trace in place of photographic recording of the galvanometer deflexion is the Leeds and Northrup instrument (Knorr and Albers, 1937 ; Machler, 1940) used by Brody and Ewing (1945).

In the operation of the Hilger Microphotometer, there are one or two points which should be noted. It is advisable to allow the projection lamp to burn for some 10 to 15 minutes before commencing readings, especially if the lamp is operated directly from an accumulator. In certain atmospheric conditions, care must be taken to avoid fogging the plate and lens during readings by moisture from the breath. This can be avoided by a loose paper collar about one inch in diameter and one inch high laid on the plate and screening the lens. It has been found too, that the Galvoscale unit requires a reasonably firm floor if it is to be operated on a table. A wall bracket mounted into the stonework of the building has proved more satisfactory.

c. The Step Sector

When a microphotometer is employed to determine the characteristic curve of a plate, the densities of sections of a spectral line that have received different exposures are plotted against the logarithms of the relative exposures. A suitably stepped spectral line can be produced in several ways. Probably the most widely used method is that employing a step sector. This is a disk (Fig. 4) from the periphery of which sections have been cut so that when it rotates in front of the slit, adjoining sections receive different exposures, generally in two-fold increments. The sector illustrated has 6 steps, giving exposures of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$ and $\frac{1}{64}$, which, with the uninterrupted light, give a spectral line which has received 7 incremental exposures. The use of a step sector to produce such an image involves the consideration of two photographic effects, namely reciprocity failure in the emulsion and the intermittency effect. The density of a photographic image is dependent on the intensity of the incident light and the time for which it is exposed, but for most emulsions there is an optimum intensity which requires a minimum exposure time to produce a given density, and for other intensities, either greater or less, a disproportionately long exposure time is required to reach this density. The *exposure* E received by a plate is defined as the product of the intensity of radiation reaching it and the exposure time, $E = It$. The density D is thus not directly proportional, when reciprocity failure occurs, to log E or log It, but the error, as far as spectrographic analysis is concerned, is small where

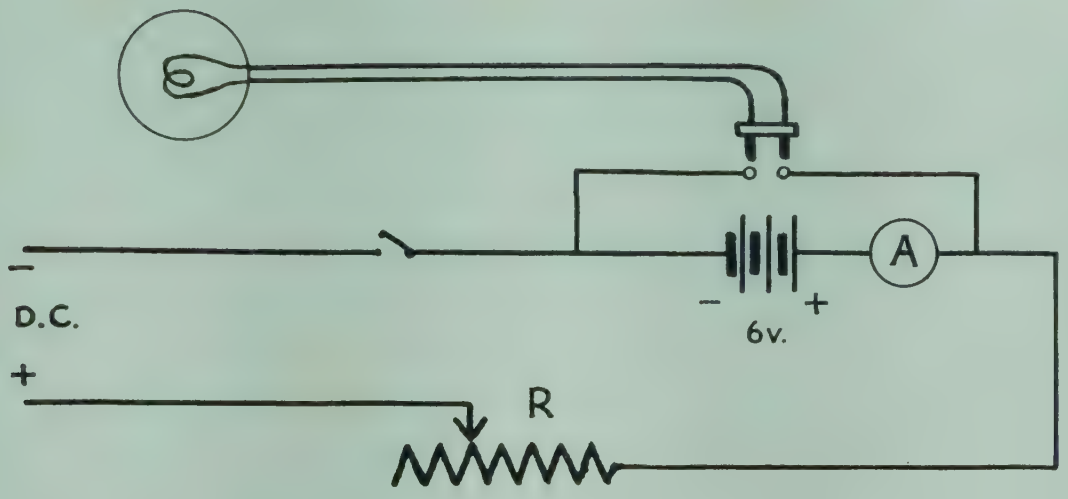


FIG. 3.—Floating battery circuit for the supply of a constant current to a microphotometer lamp

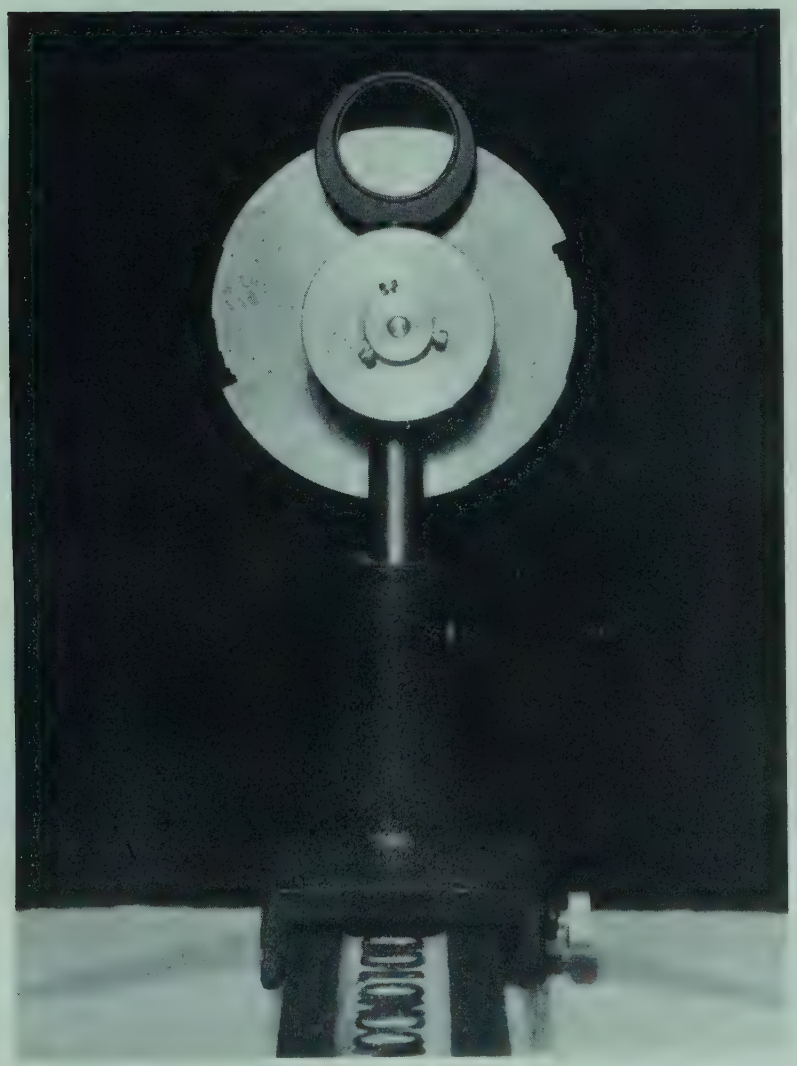


FIG. 4.—Step sector, with frequency of interruption twice its speed of rotation

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exposure times of several seconds to several minutes are concerned. The effect is illustrated for certain Kodak plates by Sawyer (1944) and Brode (1943) and its practical implication discussed by Strock (1939 b). The intermittency effect is in practice closely related to reciprocity failure. It has been shown that, at least for low frequencies of interruption, intermittent and continuous exposures of the same total energy do not produce the same density. Webb (1933 a, b) suggested that above certain frequencies of interruption the effect disappeared, these being of the order of 100 per second for one second exposures and a few flashes per second for a one hour exposure. Sawyer and Vincent (1943), on the other hand, using fast plates, failed to find this elimination of the effect. Amstein (1943) has shown that for practical purposes a fusion frequency of 80 r.p.m. exists with Ilford Ordinary plates, above which changes in sector speed can be ignored. Harrison (1939 b) makes the point that it is advantageous to have the calibration exposures and determinations made at as nearly the same speed of interruption and time of exposure as possible. It is necessary to avoid the possibility of synchronization of the step sector with an intermittent discharge such as is given by a spark or an a.c. arc. Scribner (1942) has shown that high speeds of over 1000 r.p.m. are suitable with the spark, actually using a speed of 1700 r.p.m., but practical difficulties such as vibration make high speeds undesirable if they can be avoided. Hopwood and Craggs (1947) have indicated that the intermittency effect varies at different wavelengths, using panchromatic plates.

Step sectors used at the Macaulay Institute are run at a speed of approximately 333 r.p.m., controlled by means of a stroboscope on the face of the sector. The stationary image of a ring of 18 black and 18 white sections occurs at this speed in 50 cycle a.c. lighting. The speed is not critical but it is convenient to have a simple indicator of this nature. It is, of course, not visible during an exposure whilst the d.c. arc is operating. A constant speed motor giving a speed between 250 and 500 r.p.m. would be satisfactory.

In place of a step sector which gives constant intensity and variable exposure time to the plate, a step filter may be used. The step filter is a neutral, intensity-reducing filter consisting of a quartz plate, sputtered with rhodium in strips such that the intensity of the transmitted light for different sections varies in a similar ratio to that of the exposure time variation provided by the step sector. The step filter placed before the slit thus gives an image which has received a uniform time of exposure and a variable intensity. The reciprocity failure effect discussed above is the cause of the plate calibration curves obtained by the two methods (D : log t for step sector and D : log I for step filter) being of different slopes. Strock (1939 a) points out that variable time curves are much less dependent on the intensity level of exposure—a point in favour of the step sector rather than the step filter. Other practical difficulties lie in obtaining a really neutral filter (with an even reduction of intensity over all wavelengths) with suitable step ratios. Most filters cover a narrower exposure range than the step

sector described above, whilst the liability of the filter to carry specks of dust must also be considered.

With both the step sector and the step filter, the optical set-up must be such that the spectral lines would otherwise be evenly illuminated from end to end. This is achieved by projecting an image of the source onto the collimator lens of the spectrograph by means of a spherical lens immediately in front of the slit and inserting the sector or filter between the lens and the slit. More complicated lens or lens-mirror systems have been proposed (see p. 58).

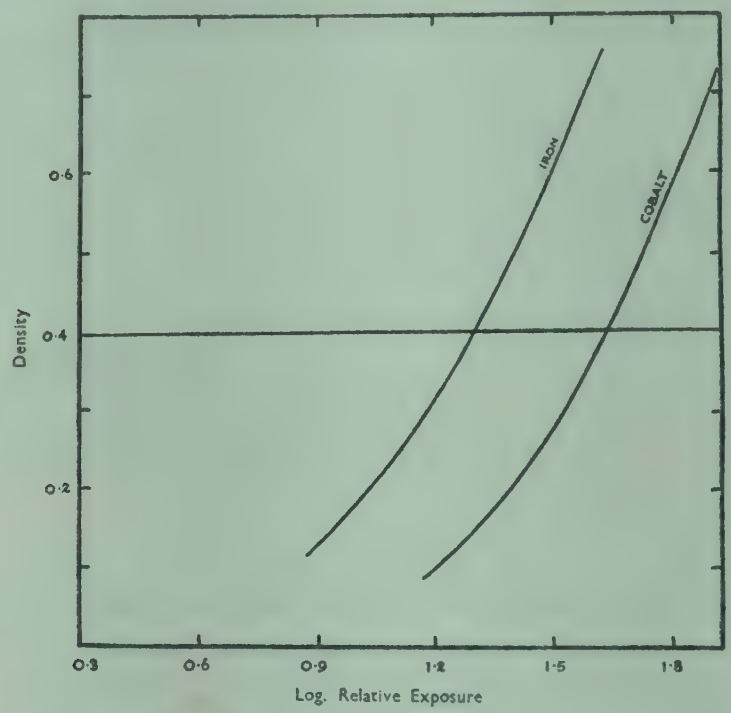

FIG. 5.—Blackening curves for cobalt (10 p.p.m.) [T] and iron (5% Fe_2O_3) [S] in an alumina matrix, for the lines Co 3453.51A and Fe 3451.92A.

When the characteristic curve of a plate is determined for a monochromatic radiation by means of the microphotometer reading of a stepped image of a single spectral line, curves such as those illustrated in Fig. 5 are obtained. It is seen that for densities below 0.3 the slope of the curve is low, but above this value the curve is steeper and practically a straight line. This straight line portion constitutes the useful range of the plate for spectrographic work. The upper limit is not seen, as the practical difficulty of obtaining accurate microphotometer readings at high densities (involving readings of less than one tenth of the full scale deflexion of the galvanometer) restricts the useful range at its upper end to a density of 1.0. The effect of microphotometer adjustment (slit width and focusing) on the calibration curve has been discussed by Coates and Amstein (1942 b) who have shown that variations in the length of the straight line portion of the curve found for the same type of plate by different workers may be ascribed to this factor.

In quantitative spectrographic analysis, the density of the image of the spectral line of the element being determined is the property which is measured and related, through an intensity relationship (obtained, for instance, from a characteristic curve), to the amount of the element in the source. The experimental conditions should be so arranged that the sole cause of intensity variation in the line in question is its concentration in the source, but, as will be seen, this condition is difficult of attainment.

d. Methods of Photometry

The simplest method of photometry is merely to plot the galvanometer deflexion for the line being measured against the logarithm of the concentration of the element being determined, as has been done by Brunstetter, Myers, Wilkins and Hein (1939). It is essential, if this be done, to have source conditions completely standardized and to carry on each plate, in addition to the unknown samples, standard mixtures corresponding closely in composition to the materials being analysed. Even with all possible precautions this technique is generally considered unsatisfactory. Besides being wasteful of standard material and plate space, it depends on a source stability which is generally not obtainable in the arc or spark.

A method only slightly more elaborate has been shown by Lundegårdh (1934) to be satisfactory for flame spectrograms, where the source can be strictly controlled and the background of continuous radiation is moderately strong and reproducible. The value for the transmission of the line itself, freed from the background on which it is superimposed, is obtained by taking the ratio of the galvanometer deflexions of line plus background and of background alone, the deflexion for total blackness being set at zero. No clear plate reading is necessary. Calibration curves are then drawn with this ratio plotted against concentration or, alternatively, the logarithm of this ratio against concentration (Lundegårdh, 1938 a). This method of evaluation is adequate for the Lundegårdh flame spectrographic method and superior to the use of the difference of the galvanometer deflexions, which has little or no theoretical justification (Mitchell, 1941 ; Ells, 1941 ; Cholak and Hubbard, 1944 b). It is doubtful if the reproducibility of an arc source is generally sufficient to permit of the use of this method although Ewing, Wilson and Hibbard (1937) and Hibbard (1941) describe a modification and it has been used for analyses of plant ash and rocks by P. H. Lundegårdh (1946 a, b).

A great improvement in accuracy can be obtained by the use of an internal standard, which is some suitable element present in the sample in known amount, so that a relationship between the intensities of the lines of this element and those of the element being determined can be established. The introduction of an internal standard permits the standard samples and the unknowns to be carried on different plates and source variations to be compensated, provided the internal standard is suitable and responds similarly to the unknown to source variations. This factor is discussed

further in Chapter 6. The internal standard principle in its earliest form is illustrated by the homologous line pairs of Gerlach and Schweitzer (1930 a). This visual comparison method entailed the presence of a line-rich element in constant amount. Then, for each concentration step in the element to be determined, a line of the internal standard identical in density to one of the unknown element could be found. Twyman and Hitchin (1931), using a logarithmic sector, pointed out that the logarithm of the ratio of the relative intensities of the two lines in question is given by the difference in their lengths, and plotted this against percentage composition. The logarithmic sector is a rotating disk in front of the slit, cut at the periphery so that the exposure given to the slit varies logarithmically along its length from continuous illumination to zero exposure. Measurement of the length of the line recorded on the plate gives a measure of its intensity (Scheibe and Neuhäuser, 1928 ; Twyman and Simeon, 1930). This method, liable to subjective errors in the measurement of the line length, has been superseded practically completely by photometric measurement.

The use of the microphotometer with an internal standard is described in its simplest form by Barker (1939) who takes the logarithm of the ratio of the galvanometer deflexions for the trace element and internal standard lines and, in the case of standards, plots this, which is actually log opacity ratio, against the percentage of the trace constituent. Barker is dealing with steels in which the iron can be taken an as internal standard of fixed content, but with biological materials the selection of an internal standard is more difficult, as no component is present in constant amount. The alternatives are to add, in constant amount, an element not already present, or to use an element present in known but variable amount. The addition of a constant content of an element is illustrated by work of Cholak (1937), who determined Bi in biological material by adding Zn as internal standard, plotting the opacity ratios of Bi to Zn (i.e., the ratios of the galvanometer deflexions) against Bi concentration. For higher contents the density of the Bi line, corrected for variations in the density of the Zn line, is plotted against the logarithm of the concentration. The use of opacities at low and densities at higher concentrations is frequently of use in avoiding a flat toe in the working curve.

There are advantages from the standpoint of accuracy in making all the measurements on a photographic plate at the same density, in other words, by so varying the exposure given to the plate that weak and strong lines can be read at the same density, this being at a point on the straight line or useful range portion of the characteristic curve. This can be achieved most simply by placing a rotating step sector or step filter at the slit. Thus the step sector or step filter has a double use in cases where each sample examined is exposed so as to produce a stepped spectrogram. Before this method is considered, however, it is necessary to consider the use of the step sector as a means of plate calibration when it is applied to only one spectrogram per plate. This type of method involves the determination of the plate calibration curve for a line with a wavelength in the neighbourhood

of those being determined, and thus of the same slope. This curve gives a density to log relative exposure relationship, and from it a measure of the intensity of any line can be obtained from its density. One weakness of the method lies in its dependence on a single microphotometer reading, which, for strong or weak lines, may be off the straight line portion of the curve. Thus the concentration range available over which the full accuracy can be obtained is limited.

Dieke and Crosswhite (1943) propose using for plate calibration a group of iron lines ending in the z^7D state in the wavelength region 3150-3250A, as these have a lower level which is above the ground state a^5D of Fe. These lines have intensity ratios independent of the mode of excitation and do not suffer from self reversal. When a series of such lines of known relative intensities is read, the results can be employed as a plate calibration curve. The classification of Fe lines has been given by Russell and Moore (1944) and from their tables, groups of suitable lines for this purpose could be selected. Plate calibration can thus be obtained from the sample being analysed without the use of a step sector.

Scribner (1942) used the step sector for all exposures and read two concurrent steps for each line, converting to log I values through a calibration curve, with the step factor correction applied. From this the ratio of log relative intensities of the internal standard and analyses lines was obtained. In his photometry Scribner followed Thomson and Duffendack (1933) in using a galvanometer scale with a zero full scale deflexion and a dark reading of 310 mm., the galvanometer reading being recorded as blackening and plotted against the logarithm of relative exposure (from a step sector) to give the calibration curve. Scribner simplified the evaluation of his results by means of a graphical calculator.

The reliability of the photometric evaluation can be improved by drawing for each line measured its own characteristic curve, by reading three steps which give points on or near the straight line portion of the curve. With the Hilger Microphotometer full scale deflexion of 50, this involves 3 readings covering deflexions of 5 to 25 or densities of 1.0 to 0.3. The readings for analysis line and internal standard are then converted to densities by means of the table (Appendix I) by Mitchell and Scott (1943 b) and plotted on suitable graph paper. A convenient size is 23×18 cm. in millimeters, with the sector steps 3 cm. apart, corresponding to the logarithm of the relative exposure $\log 2 = 0.30$. When two lines of differing intensities are plotted in this manner they appear as parallel curves as shown in Fig. 5, their position along the abcissa depending on their relative intensities. A weak line is read in the steps receiving the longest exposure times and appears close to the right hand side of the diagram. As the intensity of a line increases its curve passes across the diagram from right to left. By means of these characteristic curves it is possible to make all the determinations on the basis of one photographic density. From Fig. 5 it is possible to find the exposure time which it is necessary to give to any line to give

any desired density, say D = 0.4, whilst the separation between the curves for any two lines is a measure of the ratio of the exposure times needed to give that density. Thus if S be the curve for an internal standard line and T that for an analysis line, the separation is a measure of their log relative intensities and may in practice be measured in any convenient units, being taken as negative when the analysis line is weaker than and lies to the right of the internal standard, and positive when it is stronger than the internal standard. When a series of standard mixtures containing a constant amount of the internal standard and increments of the analysis element is examined, curve T moves to the left as the content of the latter increases. The working curve for analytical purposes can then be determined by plotting the value for the separation against the logarithm of the concentration of the analysis element, as in Fig. 6. This method of photometry has been quite widely used, for instance by Hultgren (1932), Breckpot (1933, 1939), Preuss (1935, 1938) and Strock (1936 a).

The difficulty of finding, in biological and similar samples, a suitable internal standard present in constant amount, has already been mentioned. This problem has been tackled by Davidson and Mitchell (1940 a) by means of the variable internal standard method which has since 1940 been used at the Macaulay Institute for the determination of trace constituents in soil and plant materials. This method involves in the first place the production of a series of working curves from sets of standard mixtures containing increments of analysis elements in matrices similar in composition to the samples to be analysed, but with increments of the internal standard, which is generally iron, from one set to the next. The preparation of the standard mixtures is discussed elsewhere (see p. 81), but a suitable series of matrices might contain, for our work involving prior concentration

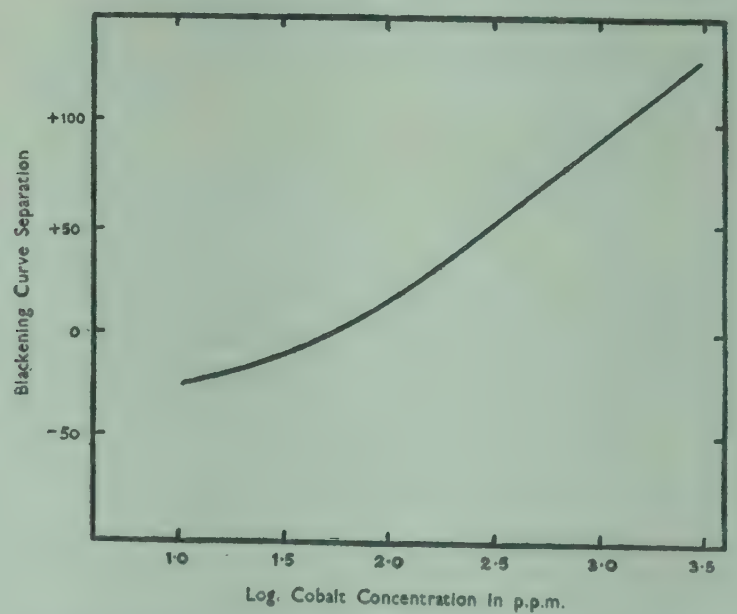

FIG. 6.—Working curve for the determination of cobalt in an alumina matrix containing 5% Fe_2O_3, without correction for the effect of spectral background

into an alumina matrix, 2.0, 3.5, 5.0, 7.0, 10.0, 13.0, 18.0 and 25.0% of Fe_2O_3 in Al_2O_3, with, for each Fe_2O_3 content, a dilution series of standard mixtures containing from 1% down to 1 p.p.m. in steps of $\sqrt{10}$ of such analysis elements as Co, Ni, Mo, Cr, V, Ti, Sn, Pb, etc. A series of working curves as shown in Fig. 7 is obtained from these standards. These are actual curves obtained by Dr. R. O. Scott for Co in an Al_2O_3 matrix. These curves are seen to be parallel, with a constant vertical separation at all contents of the analysis element. This means that the relative position of Curve S in Fig. 5 is constant for one content of the internal standard, but is displaced a constant amount for a given change in the internal standard, irrespective of the content of the analysis element, i.e., of the position of T. It is of course only the relative positions of S and T that are being considered. Their absolute positions are liable to slight variations due to such effects as amount of material in the electrode, and other source variables, and also to slight photographic effects due to development differences if all the spectrograms are not carried on one plate.

The mean value for the vertical displacement of a working curve due to change in internal standard content is obtained by measuring the displacement at close intervals : say at 1 cm. horizontal distances if the log concentration scale from 10 to 3162 p.p.m. covers 25 cm. The values so

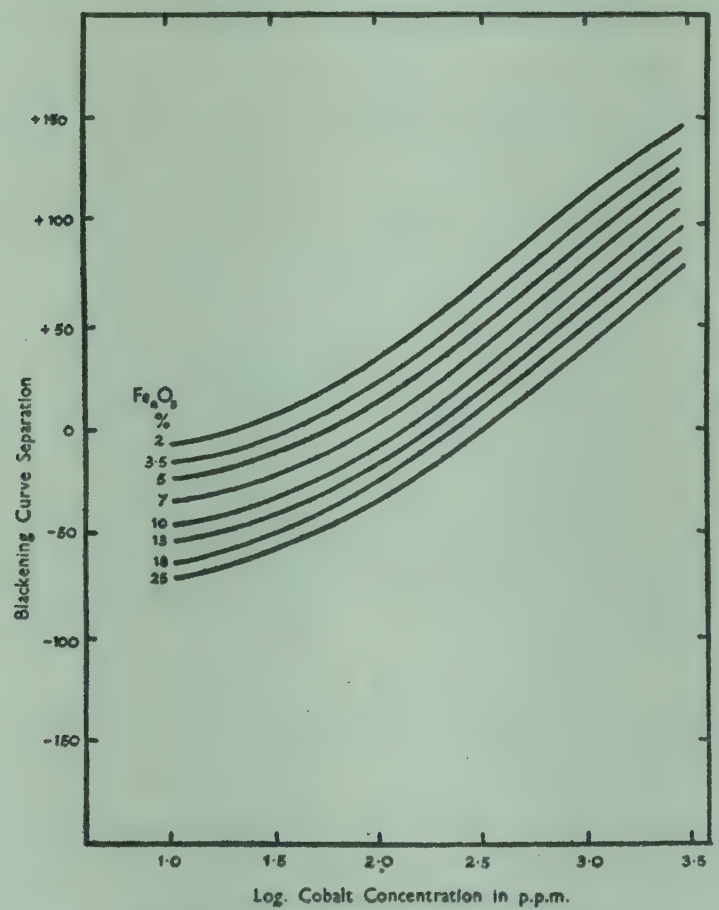

FIG. 7.—Series of working curves for cobalt in an alumina matrix with incremental contents of Fe_2O_3, without correction for the effect of spectral background

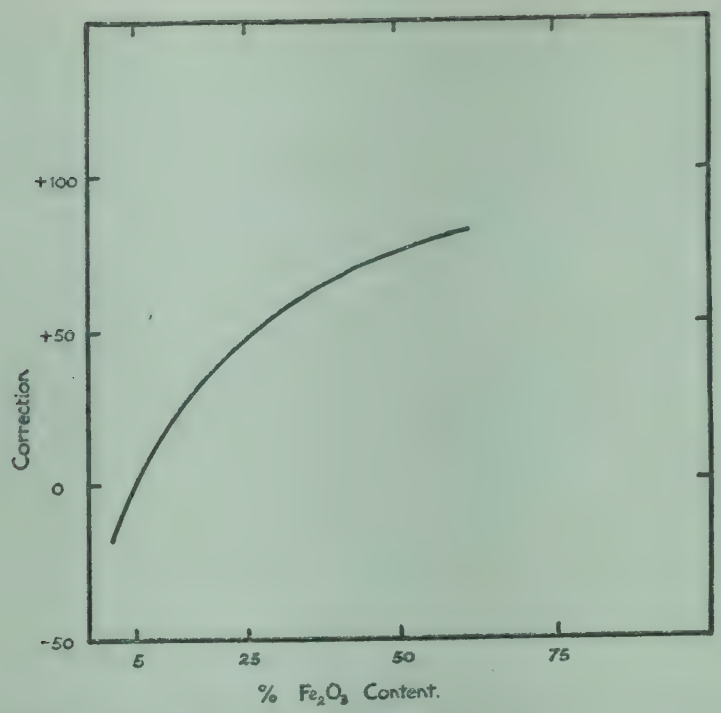

FIG. 8.—Correction curve for the variable internal standard method, permitting the use of a single working curve

obtained are plotted against the Fe, or generally in our case the Fe_2O_3 content, to give a curve of the type illustrated in Fig. 8. It is advisable in the variable internal standard method for the measurements to be made to the working curve which has an Fe content nearest the general run of samples to be analysed : 5% Fe_2O_3 has been selected in our work. Then the displacement, or the *correction* as it may be called, for 5% Fe_2O_3 is zero, whilst that for lower contents is negative and for higher contents positive. From Fig. 8 can be read off a value for the correction for any Fe_2O_3 content between the limits for which working curves were obtained. Once this correction curve is made, all the working curves can be discarded except that chosen as the standard working curve : 5% Fe_2O_3. To determine the content of an analysis element in any sample it is necessary only to know its Fe_2O_3 content and the separation of its Fe and analysis element blackening curves. To this separation is added the correction for the Fe_2O_3 content, obtained from the correction curve of Fig. 8, and the corrected separation applied to the working curve of Fig. 6 to obtain the logarithm of the concentration of the analysis element.

The data required for this evaluation are conveniently carried on an analysis card similar to that shown in Fig. 9. The heading carries information regarding the filing number of the plate, the lines being measured, the full scale (clear plate) galvanometer setting, the density at which the blackening curve separations are to be read, and the nature of the matrix of the materials in which the analyses are being made, for, as will be seen, different working curves may be required for different matrices. The body of the card has room for results for 6 spectrograms, the number normally

ELEMENT - Mo (3170·34) I_0 = 50 PLATE NO. 4217

COMPARISON - Fe (3116·63) S = 0·4 CURVE Al_2O_3

Sample	I	Log $\frac{I_0}{I}$	I_c	Log $\frac{I_0}{I_c}$	Separation	% Comparis'n	Correction	Corrected Separation	Log p.p.m.	p.p.m.
859										
	4·2	1·076								
	10·2	690	7·0	854	−14	8·3	+20	+6	2·430	269
	21·2	373	15·5	509						
			29·0	236						
860										
	5·0	1·000								
	11·6	635								
	22·6	345	7·7	813	−43	7·5	+15·5	−27·5	2·030	107
			17·1	466						
			30·6	213						
861	4·4	1·056								
	10·5	678								
	20·9	379	6·0	921	−48	5·6	+4·5	−43·5	1·845	70
			13·9	556						
			25·6	291						
867										
			5·8	936						
			13·4	572	+55·5	4·5	−3·5	+52	3·025	1059
	6·0	921	26·3	279						
	15·0	523								
	28·5	244								
919										
			9·0	745	+47·5	7·1	+13·5	+61	3·175	1496
	4·5	1·046	19·6	407						
	13·0	585	33·5	174						
	24·4	312								
920										
			7·4	830	+50·5	6·9	+12·5	+63	3·215	1641
	4·1	1·086	17·6	454						
	10·6	674	31·6	199						
	21·5	367								

FIG. 9.—A typical analysis card for the determination of molybdenum in an alumina matrix, without background correction

carried on one plate, with a space for a galvanometer reading for each of the 7 steps, and for the density value calculated for this reading (obtained from the Table of Appendix I). The succeeding columns carry the blackening curve separation, the Fe_2O_3 content, the correction for this content, the corrected separation, the log concentration and the final content in parts

per million. A card of this nature helps to prevent errors during the evaluation of the results and facilitates subsequent reference.

This method has been employed successfully for the determination of Co, Ni, Mo, Cr, V, Ti, Sn, Pb, Be and Ge with Fe as internal standard, and of Zn with Cd as internal standard. Details of the wavelengths of the lines used and the concentration ranges covered are given below (see p. 88).

e. Background Correction

A factor which is ignored in the above method, as well as in the majority of the methods of photometry that have been described, is the effect of the background intensity on the spectrogram. Examination of most spectrograms shows that the lines are superimposed on a background which is appreciably darker than the general fog level (which should be negligible) of the unexposed portions of the plate emulsion. This background in arc spectrograms is generally fairly uniform over short wavelength ranges but does vary throughout the spectrum, being generally darkest in the yellow to blue region of the visible. There is occasionally, as a result of the presence of elements such as Si, a weak banded background in certain wavelength regions. This is not to be confused with the CN bands which are typical of arc spectrograms between carbon electrodes, and make determinations very difficult or impossible in their neighbourhood.

Numerous attempts have been made to work out a quick method of background correction ; probably the simplest is that of Lundegårdh (1934) which is relatively efficient for flame spectrograms. The assumptions which it is necessary to make here, as in all background correction methods, are (1) that the Lambert-Beer Law holds, namely that the density of the image produced, that of line superimposed on background, is the sum of the densities of the line and background if they could be obtained independently, i.e., $D_{L+B} = D_L + D_B$, (2) that the density of the actual background under the line can be obtained with sufficient accuracy by measurement at a suitable point in its neighbourhood, (3) that the source conditions do not cause some mutual interference between the background and line radiations : that the background radiation at the line wavelength is in fact what it would be were the line not present and that the presence of background radiation does not affect the intensity of line emission from the radiating atom.

Lundegårdh (1934) showed that the ratio of the galvanometer deflexions obtained for line + background and background images gives in fact a value for the transmission of the line freed from background, and this method does in practice give correction for quite large background fluctuations caused by the presence of extraneous elements such as Mg in the flame. As McClelland and Whalley (1941) point out, the logarithm of the ratio of the two deflexions is inversely proportional to the logarithm of the ratio of the intensity of line + background to intensity of background and is independent of the time of exposure, provided Schwarzchild's law is applic-

able. The ratio method is unjustified only when the line or background does not obey this law, which states that $D = \gamma \log It^p - \alpha$ where t is exposure time, and γ, p and α are constants, γ being the contrast factor of the plate. This occurs only when the image is over or underexposed, and even then the error is small if standards of the same nature are carried on the same plate.

Difficulties arise when background correction is attempted by some such simple method if the source is not as stable as that provided by the Lundegårdh flame, or if it is not practicable to carry comparison standards in the same plate. There is a further photographic effect which is of importance in the consideration of background interference in spectrographic analysis, although its presence must be kept in mind even when background is not a serious problem. This is the Eberhard effect (Eberhard, 1926; Strock, 1938, 1940) which according to Strock is essentially an effect associated with the penetration of the developer into the exposed emulsion. It is generally found that in practice the slope of the blackening curve is greater for a narrow line image or for the edge of a wide image than it is for the central portions of a blackened area, due, it is claimed by Strock, to the easier diffusion of the developer to the edge of the area through emulsion which does not carry a developing image. The practical result is that the blackening curve for a continuous spectrum such as is provided by the background is less steep than that for a line image. Pierce and Nachtrieb (1941) have failed to obtain any difference, but Scott's unpublished results at the Macaulay Institute have confirmed Strock's findings as far as the slope difference is concerned. The effect can, it is claimed (Sawyer, 1944), be reduced during development by vigorous agitation or brushing. The cause suggested here is not lack of developer penetration but local depletion of developer.

It is only since about 1940 that serious attempts have been made, in methods other than those using the flame, to make a correction for the effect of background. This was due to the fact that until that time most of the investigations were concerned with metals and alloys, where the background problem is not so serious as it is with non-conducting samples burnt in carbon electrodes, and because, whilst the contents encountered in biological work often entail determinations of lines which are little darker than the background itself, in metallurgical work the lines involved are generally considerably denser and well above whatever background exists.

The effect of the width of the spectrograph slit is of importance when the background effect is being considered, as the density of a line image is generally independent of the slit width over the range of slit widths normally used (*v.* Sawyer, 1944) whilst the background intensity, when due to continuous radiation, increases with slit width. Thus Follett (1936) advised the use of a narrow slit if background were present, whilst Rössler (1938) has also studied this aspect.

Bell (1938) attempted a correction for background in arc spectrograms by using the difference between the galvanometer deflexions from line + background and background. This approach is, however, unsound for sources as variable as the arc, as is that of Ewing, Wilson and Hibbard (1937) and Wilson (1942) who used the ratio of the galvanometer deflexions, following the Lundegårdh procedure.

Melvin and O'Connor (1941) and Pierce and Nachtrieb (1941) have both proposed background correction methods which incorporate the use of a blackening curve for the conversion of the density values to intensities for both line + background and background before making the background correction, the latter method being used by Cholak and Story (1942) who also discuss the problem of the presence in the electrode material of small amounts of the elements being determined. These methods mark a considerable advance in the technique of background correction, but suffer from the fact that the photometric readings are made at different densities, a factor which is of particular importance if the Eberhard effect is present. Pierce and Nachtrieb failed to find it, but at the Macaulay Institute, as already mentioned, our experience has been that the background blackening curves are somewhat less steep than those for a line image, the contrast factor increasing with the density of the line (R. O. Scott, unpublished) in conformity with the findings of Strock (1940). Scott (1944, 1946) has developed the method of Davidson and Mitchell (1940 a) by incorporating a background correction at a constant photographic density, and this method is described in some detail as it is the one recommended for all determinations where either of the lines (internal standard or analysis) being measured is near the background intensity level. In this connexion it is interesting to note the conclusion of Hasler and Kemp (1944) that weak lines can conveniently be measured if line + background intensity is 1.3 times that of the background. A background correction is not necessary if internal standard and analysis lines are of equal intensity.

For the method involving correction for background at a constant density the photometry for the analysis and internal standard lines follows that previously described for the blackening curve separation method, but is extended by the measurement of as many steps of the background in the neighbourhood of the two lines as is feasible. Often only two steps are readable, and the deflexion corresponding to the density at which the measurement is being made may not be obtained. In this event it is necessary to extrapolate the blackening curve. From the densities corresponding to the galvanometer deflexions the blackening curves are drawn, as in Fig. 10. The points at which the curves cut the selected density level give the logarithms of the relative exposure times which are required to produce these densities, or the logarithms of the relative intensities of line + background and background. The logarithms of the relative exposures run from 0 in the first ($\frac{1}{64}$ exposure) step, by increments of 0.3, to 1.8 in the seventh (continuously exposed) step, whilst the logarithms of the relative

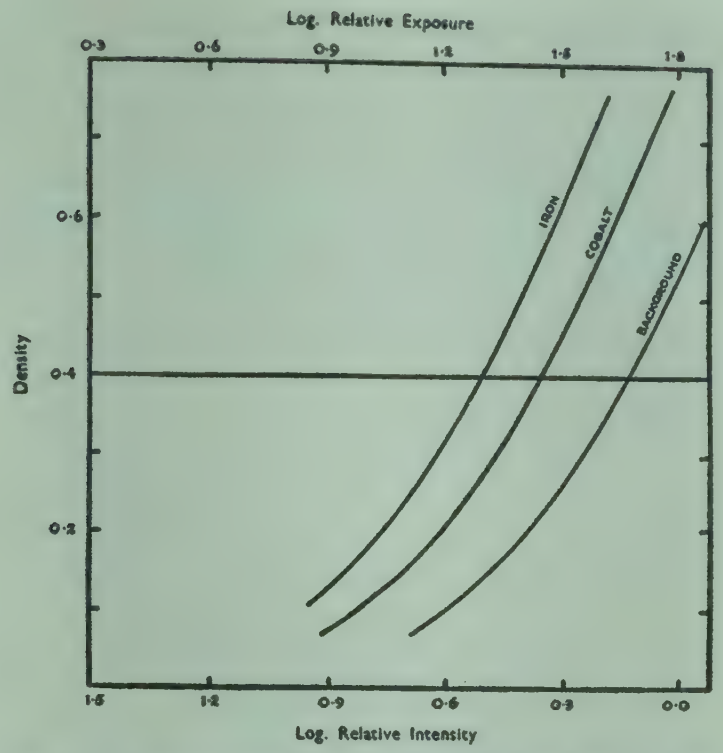

FIG. 10.—Blackening curves for cobalt (30 p.p.m.), iron (5% Fe_2O_3) and background, for the lines Co 3453.51A and Fe 3451.92A in an alumina matrix

intensities run in the opposite fashion from 1.8 at the left side of the diagram, corresponding to a measurement in the seventh step, to 0 on the right hand side corresponding to the first step. Once again a millimeter scale with step intervals of 3 cm. (= 0.3 units of log relative intensity) is most convenient. The log relative intensities of line + background and background can now be read off on the appropriate scale and from this the log relative intensity of the line itself calculated. Where it is required to determine the ratio of the log relative intensities for the analysis (I_T) and internal standard (I_S) lines, this is a tedious process involving numerous references to logarithm tables, but it can be greatly shortened by the use of gaussian or subtractive logarithms (Mitchell and Scott, 1943a), offprints of a suitable table being available from the Macaulay Institute. An even greater simplification is achieved by the method suggested by Farmer (Mitchell, Scott and Farmer, 1944, 1946). In the use of subtractive logarithms, if $\log (I_T + I_B) - \log I_B = \delta_T$ and the subtraction logarithm of δ_T is γ_T*, then $\log I_T = \log (I_T + I_B) - \gamma_T$, and similarly $\log I_S = \log (I_S + I_B) - \gamma_S$ where I_B is the background intensity. From the above $\log I_T = \log (I_T + I_B) - \gamma_T = (\delta - \gamma)_T + \log I_B$, and similarly $\log I_S = (\delta - \gamma)_S + \log I_B$ so that $\log (I_T/I_S) = (\delta - \gamma)_T - (\delta - \gamma)_S$ where the background is the same for both lines. Now δ is actually the separation of the blackening curve for the line + background from that of the background, as illustrated in Fig. 10, whilst $(\delta - \gamma)$ is easily worked out from a table of subtractive logarithms, and a table giving values of $(\delta - \gamma)$ for values of δ is given in

* Not to be confused with the contrast factor of the plate emulsion.

Appendix II. δ_T and δ_S can thus be read off directly from the blackening curves at the appropriate density, $(\delta - \gamma)_T$ and $(\delta - \gamma)_S$ obtained from Appendix II ; log (I_T/I_S) follows by simple subtraction. If the lines are on backgrounds of different intensities, a blackening curve is drawn for each background and the separation read to the appropriate background. To the difference of the $(\delta - \gamma)$ values so obtained is added the separation between the backgrounds, measured in the same manner, this being taken as

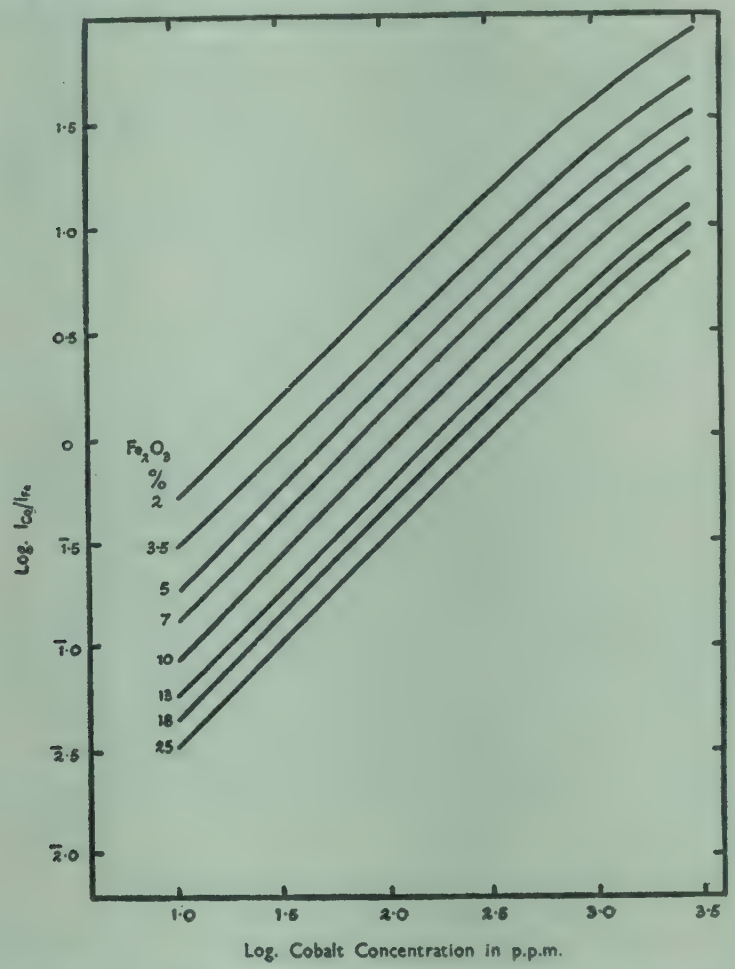

FIG. 11.—Series of working curves for cobalt in an alumina matrix with incremental contents of Fe_2O_3, with correction for spectral background

positive when the background of the analysis line is the stronger. A table similar to that of Appendix II has been given by Honerjäger-Sohm and Kaiser (1944) for an arbitrary background correction method.

Once the value of log (I_T/I_S) is obtained, it is treated in the same manner as the value for the blackening curve separation was treated in the previous method. For standard mixtures, the values of log (I_T/I_S) are plotted against the logarithm of the concentration to give working curves, one being drawn for each internal standard content. A typical series of working curves is seen in Fig. 11, these being obtained from the same spectrograms as those uncorrected for background in Fig. 7. It will be seen that the correction for background has removed the pronounced toe of the working curves at

low concentrations of the analysis element, and that, except at very high contents of the analysis element, they are now straight lines at an angle of approximately 45° when the appropriate scales, namely one log (I_T/I_S) unit = one log concentration unit, are chosen. The toe is thus shown to be due to background effect. The slight falling off in slope at high contents can be ascribed to self reversal, as the line used for the determination ends on its ground state. This often cannot be avoided in biological trace element work where the utmost possible sensitivity is required.

Values for the displacement of the curves for different internal standard contents from the standard working curve are obtained as previously

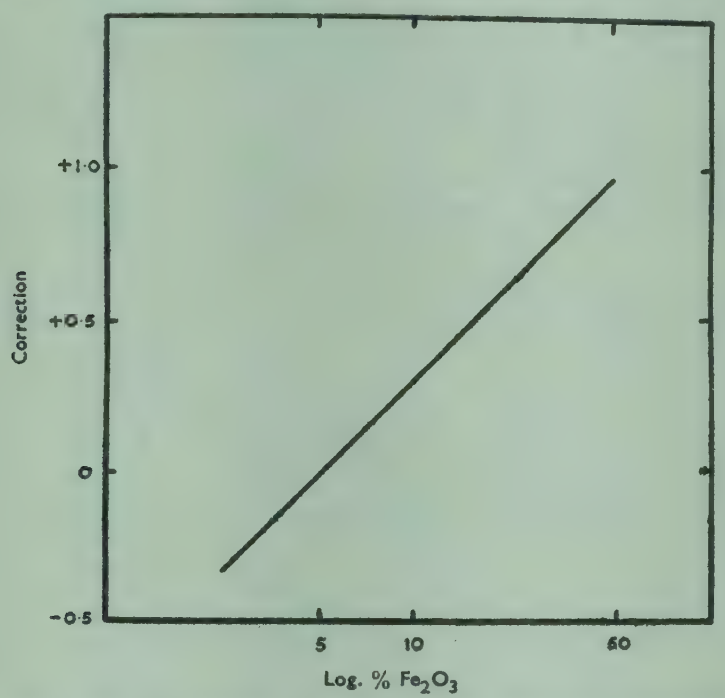

FIG. 12.—Correction curve for the variable internal standard method, after correction for the effect of spectral background, using a logarithmic scale for the internal standard content

described and the correction curve drawn. In practice it is most convenient to use a linear Fe_2O_3 scale as previously, but if the displacement be plotted against log Fe_2O_3 content the correction curve takes the same form as the working curve, a straight line at an angle of approximately 45°, as it is essentially a working curve for Fe_2O_3 using the analysis element as internal standard (Fig. 12).

In the evaluation of the results of determinations, to the value for log I_T/I_S obtained as described above, the correction for the appropriate Fe_2O_3 content is applied as in the previous method, and the corrected value gives the log concentration from the working curve. The lay-out of the analysis card used for background correction determinations is shown in Fig. 13. The fourth column carries the galvanometer and density values for one or both of the background readings whilst further calculations are made in the other spaces provided.

ELEMENT - Co (3453·5) I_0 = 50 PLATE NO. 3972

COMPARISON - Fe (3451·9) S = 0·4 CURVE Al_2O_3

Sample	I	Log $\frac{I_0}{I}$	I_c	Log $\frac{I_0}{I_c}$	I_B	Log $\frac{I_0}{I_B}$			Log p.p.m.	p.p.m.
135					11·6	635	δ_{Co}	1·045		
			6·3	900	22·4	349	δ_{Fe}	0·475		
			15·6	506			$(\delta-\gamma)_{Co}$	1·004		
	6·3	900	28·0	251			$(\delta-\gamma)_{Fe}$	0·298	2·645	442
	16·2	490					Difference	0·706		
	30·8	210			Fe_2O_3	7·6%	Correction	+ 0·190		
							$\log I_c/I_{Fe}$	0·896		
136					6·3	900		1·210		
					15·2	517		0·405		
			4·5	1·046	27·6	258		1·182		
			11·5	638				0·188	2·970	933
	5·7	943	23·4	330				0·994		
	14·9	526				8·1%	+	0·225		
	26·9	269						1·219		
137					13·2	579		0·810		
			7·9	801	25·3	296		0·470		
	6·6	880	18·0	444				0·737		
	16·0	495	31·0	208				0·291	2·355	227
	29·7	226						0·446		
						7·1%	+	0·160		
								0·606		
138					9·5	721		0·410		
	6·6	880	5·8	936	20·6	385		0·490		
	15·9	498	13·8	559				0·196		
	29·2	234	26·1	282				0·291	1·925	84
								T·905		
						8·8%	+	0·265		
								0·170		
139					6·4	890		0·330		
	6·0	921	5·0	1000	15·6	506		0·380		
	14·5	538	12·6	599	28·4	246		0·056		
	27·7	257	25·1	299				0·146	1·675	47
								T·910		
						5·1%	+	0·010		
								T·920		
140					8·7	760		0·515		
	4·2	1076	7·2	842	19·5	409		0·370		
	11·6	635	16·7	476	32·8	183		0·357		
	23·0	337	29·5	229				0·128	2·080	120
								0·229		
						6·2%	+	0·100		
								0·329		

FIG. 13.—A typical analysis card for the determination of cobalt in an alumina matrix, with background correction

In practice it has been found desirable to employ this background correction method wherever the line + background density of either analysis or internal standard line falls nearly to that of the background, as is very often the case in the determination of cobalt in plant materials, even after prior chemical concentration. The fact that, after background correction,

the working curves of most elements so far examined in the cathode layer arc give working curves of $45 \pm 0.5°$ and correction curves of the same angle, as shown by Scott (1946) for Cr, Co, Ni, Ag, V, Mo, Be, Ge, Ga, Sn and Pb, suggests a possible quick means of determining an element for which full working and correction curves are not available, provided that it is known that the method can be applied to it. From one standard mixture of known internal standard and analysis element contents, a working curve can be obtained by drawing the 45° line through the point given by the log (I_T/I_S) value and the logarithm of the analysis element content. Then the logarithmic correction curve can be obtained by drawing a 45° line through the point given by zero correction and the known internal standard content of the standard mixture. As Scott (1946) has shown, in favourable conditions errors by this method are not greatly in excess of those obtained from determined working curves. The standard mixture chosen should approximate as closely as possible in composition to the unknown : hence a spectrogram of the latter should first be examined visually and an appropriate standard mixture employed.

The 45° working curve, i.e., a curve with a slope of unity, can be anticipated on theoretical grounds and has been obtained by numerous other workers (e.g. Hasler and Kemp, 1944 ; Boer, 1940 ; Nachtrieb, Johnson and Dress, 1943 ; Hampton and Campbell, 1944) except at contents where reversal effects reduce the slope of the curve. Scott (1946) appears to have obtained such curves much more generally than other workers, possibly because the amounts of material employed in the cathode layer technique are less than are often employed in other arc methods, and because its passage through the arc column is slow owing to the electrode shape. Self reversal effects are thereby kept to a minimum.

The advantages gained by the constant blackening methods of photometry are that, where the Eberhard effect does not exist, and the blackening curves are parallel, the variations in the degree of development within wide limits are not of practical importance, whilst provided the development is reasonably constant from plate to plate, the Eberhard effect, should it exist, can be ignored. Similarly the effect of reciprocity failure and intermittency are much better compensated in this manner than by single value density measurements converted to intensities through a blackening curve. The three readings per line cut out chances of misreading and effects of slight plate faults, which are easily detected by an abnormal blackening curve slope, without increasing the reading time unduly, as much of the time involved is spent in the initial adjustment of the line in the microphotometer.

f. Other Methods of Photometry and Calculation

Mention must be made of the external standard method of Hampton and Campbell (1944) in which each plate is calibrated by burning 10 mg. of Co_2O_3 to completion in a d.c. arc, and developing to a fixed γ of 1.0. The galvanometer deflexion for any analysis line is converted to intensity in terms of " cobalt units," no internal standard being employed. Slavin

(1938) has also developed a method based on the spectral energy developed by complete combustion of a known quantity of material, unknowns being measured through a secondary standard such as a mercury arc lamp or an iron globule arc (Slavin, 1940 b, 1941).

The quantitative addition method involves the determination of the content of a trace constituent by the comparison of the intensity of the line of the unknown with that of the same material to which a known amount of the trace constituent has been added, so that contents of x and (x + a), where a is the known addition, are present in the two samples analysed. Oertel (1944 a) suggests the use of two known additions, other workers (Hasler, 1938 ; Nelson, Hamm and Tsiang, 1943; Foster and Horton, 1937 ; Foster, Langstroth and McRae, 1935) have used variations of the method.

The use of the line width as a method of quantitative analysis has been considered by Coheur (1946) following Gerlach and Rollwagen (1937). The method is stated to be practical and accurate, and independent of development conditions or exposure time. It has been employed also by Eisenlohr and Alexy (1937).

The concentration working curve can be combined with the variation of the internal standard content in the concentration-ratio method, in which the logarithms of the relative intensities of analysis and internal standard lines (or other equivalent value, such as blackening curve separation) are plotted against the logarithms of the ratios of the concentrations of the analysis element and the internal standard. This method, which has been used by Kvalheim (1941), Coulliette (1943), and Churchill and Russell (1945), holds only over the straight line portion of working curves, and where the working curves for different internal standard contents are parallel, as has been pointed out by Scott (1946).

The time required in the evaluation of photometric data may be shortened by various devices, generally with some slight loss of accuracy. A logarithmic galvanometer scale can be employed in place of a linear scale, so obtaining density values directly. Sinclair (1944) transferred the projection of a background corrected log intensity ratio working curve on to a scale of the same dimensions as the galvanometer scale and was thus able to read concentrations directly. Henderson-Hamilton and Lourie (1945) employed a curved galvanometer scale for the same purpose.

The use of graphical plate calculators to reduce the arithmetical calculations necessary in the conversion of density values into concentrations has been described by numerous workers, including Owens (1938 a), Langstroth and McRae (1938), King (1942), Cheng (1943), Vanselow and Liebig (1944), Bromelle and Clayton (1944), Churchill (1944) and British Aluminium Company (1943). A graphical plate calculator is essentially a combined working curve and slide rule in which the relative positions of the intensity and concentration scales are first adjusted to suit the plate calibration curve, after which the concentrations can be read off directly from the cursor. Variation in internal standard content can be allowed for by a scale on the cursor, following Hasler, Harvey and Dietert (1943).

Chapter 4

FLAME EMISSION METHODS

a. General

The limited thermal energy available in the flame restricts to those with easily excited atoms the elements which can be observed or determined by means of their flame spectra. As the alkali and alkaline earth metals, together with certain others such as copper, manganese, iron, cobalt, nickel and chromium are fairly sensitive, flame methods have quite widespread applications. The simplicity of flame spectrograms is an appreciable advantage when high concentrations of line-rich elements such as iron are present. It is less difficult in the flame than in most other sources to establish reproducible conditions and so to obtain accurate quantitative determinations. Flame methods are, for most elements, not so sensitive as arc methods, and generally do not provide determinations of trace quantities in biological materials.

The classical qualitative method of introducing material into the flame is by means of a moistened platinum wire (Bunsen, 1859; Kirchhoff and Bunsen, 1860). The first of many attempts to improve the sensitivity and reproducibility was probably that of Mitscherlich (1862) who fed solution into the flame from a glass tube along a bundle of platinum wires. Eder and Valenta (1893) used a platinum gauze disk, driven by clockwork, that passed through the solution being analysed before entering the flame. By means of a platinum spiral which carried solution into the flame, Gooch and Hart (1891) and Gooch and Phinney (1892) developed a quantitative method for the determination of K and Rb, whilst more recently Heller, Peh and Gürtler (1934) have determined Rb in extracts of potato ash by introducing the solution on a platinum wire fed by capillary action from a porcelain boat. These early methods of mechanical introduction of solution (or, in some instances, solid) into the flame resemble in some respects that developed by Ramage (1929) who introduced a spill of filter paper carrying powder or a dried solution.

The use of a solution spray permits the distribution of the material through the body of the flame rather than its introduction at a point. The earliest method of Kirchhoff and Bunsen was by the spray from an acidified solution to which Zn was added. This method has been recently examined by Török (1939, 1940) who used also Al + KOH as a source of a hydrogen spray and HCl + $(NH_4)_2CO_3$ for a carbon dioxide spray. Gouy (1879)

developed an atomizer employing compressed air, which carried a spray of the solution into the flame. This provided the basis for Lundegårdh's (1928) early work and has been considerably improved and simplified. A third method of spray production is the electrolytic method used by Klemperer (1910), but this method does not appear to have been developed further.

Quantitative analysis by flame methods can for practical purposes be divided into the two distinct categories, of which the Lundegårdh and Ramage techniques are the most widely used, and these will be discussed in more detail. Their applications have been to the determination of the exchangeable or easily soluble alkali and alkaline earth cations in soils and to the same elements and manganese in solutions of plant materials.

b. The Lundegårdh Flame Emission Method

In the Lundegårdh method, a solution containing the elements to be determined is atomized by means of a jet of compressed air and carried as a spray into an acetylene flame. Precautions are taken to establish reproducibility by controlling the pressure of air and acetylene. The air-acetylene flame is very hot, but it serves no purpose to discuss the maximum temperature reached at any point, for it must vary between outer and inner zones of the flame, and, as the atoms introduced into the flame are intimately mixed with it, emission from all temperature zones at the chosen height reaches the spectrograph.

The acetylene flame spectrum shows, like the outer cones of most organic flames, principally the OH-band spectrum and the continuum of dissociating CO molecules. Most characteristic is the OH-band head at 3064A. The system consists of four band heads degraded to the red and shows open rotational fine structure. The 0,0 R_2, R_1, Q_2 and Q_1 branches have their heads at 3063.6, 3067.2, 3078 and 3089A, the last three being less apparent as they are much overlapped by bands from higher frequency heads. To the same OH system belong the heads near 2810A, with 1,0 R_2, R_1 and Q_1 heads at 2811.3, 2816.0 and 2829.0A, (ascribed by Lundegårdh, 1936, to CH) and the much weaker bands below this wavelength with the 3,1 R_2 head at 2677.3A and the 2,0 R_2 head at 2608.5A. Towards the red, the banded structure of the spectrum disappears about 3200A with the relatively wide slit employed in the Lundegårdh technique (0.04 mm.) and in its place occurs the continuous spectrum of the carbon monoxide flame which stretches from approximately 3000 to 5000A, with its greatest intensity about 4000A. This continuous background is of great importance in the Lundegårdh method, as it is employed as a form of internal standard, or measure of flame constancy. Superimposed on this background can be seen the faint CH bands at 4312.5A, degraded to the violet, and, generally very faintly, four or five heads of the C_2 Swan system from 4737.1 to 4678.6A, degraded to the violet. These bands which are produced in reducing conditions are very strong in the spectrum of the inner cone, as are the u.v. bands already noted, and also further bands in the u.v. and visible.

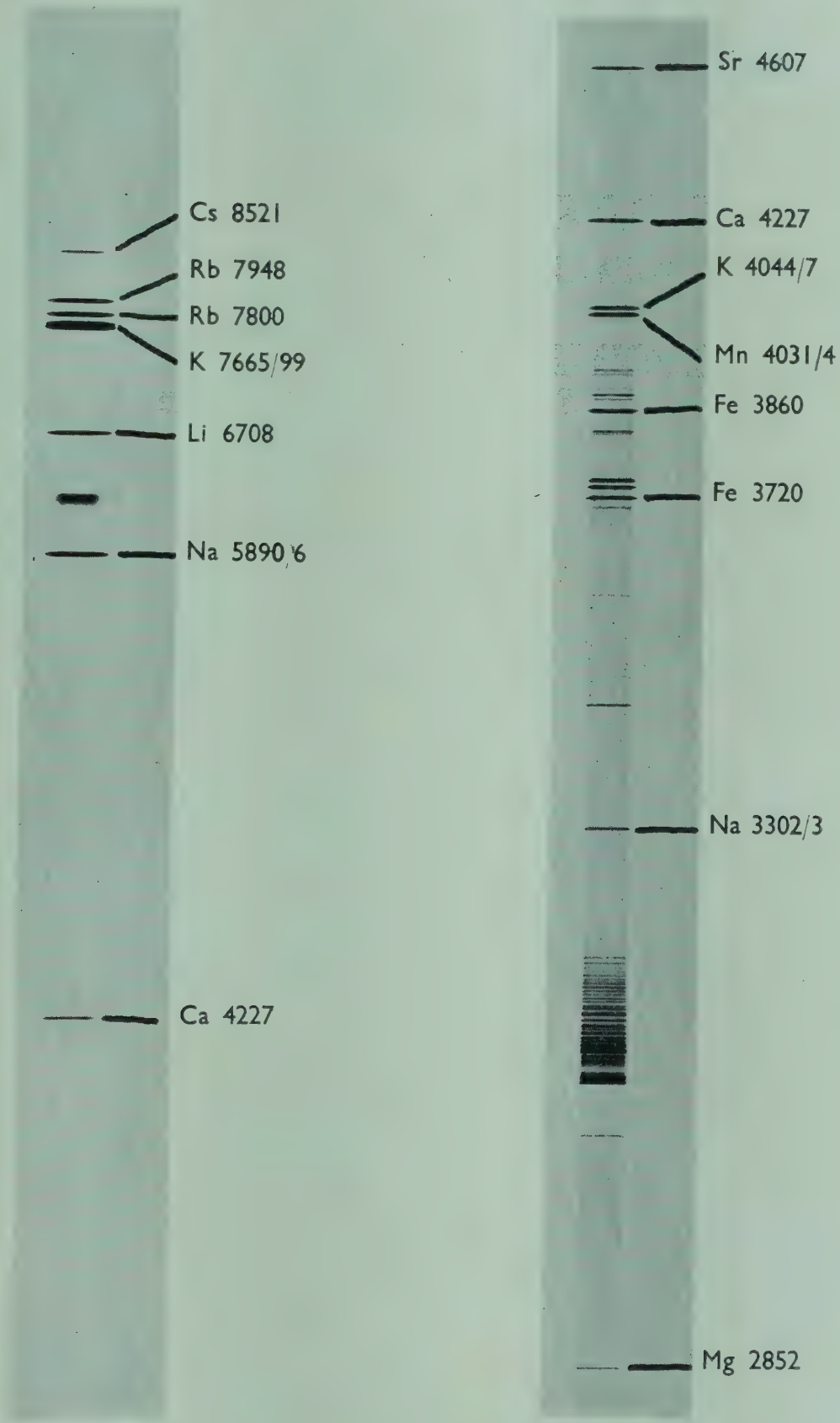

FIG. 14.—Lundegårdh flame spectrogram. From 2800 to 4800A on Ilford Zenith and from 4200 to 8600A on Kodak N.I plates

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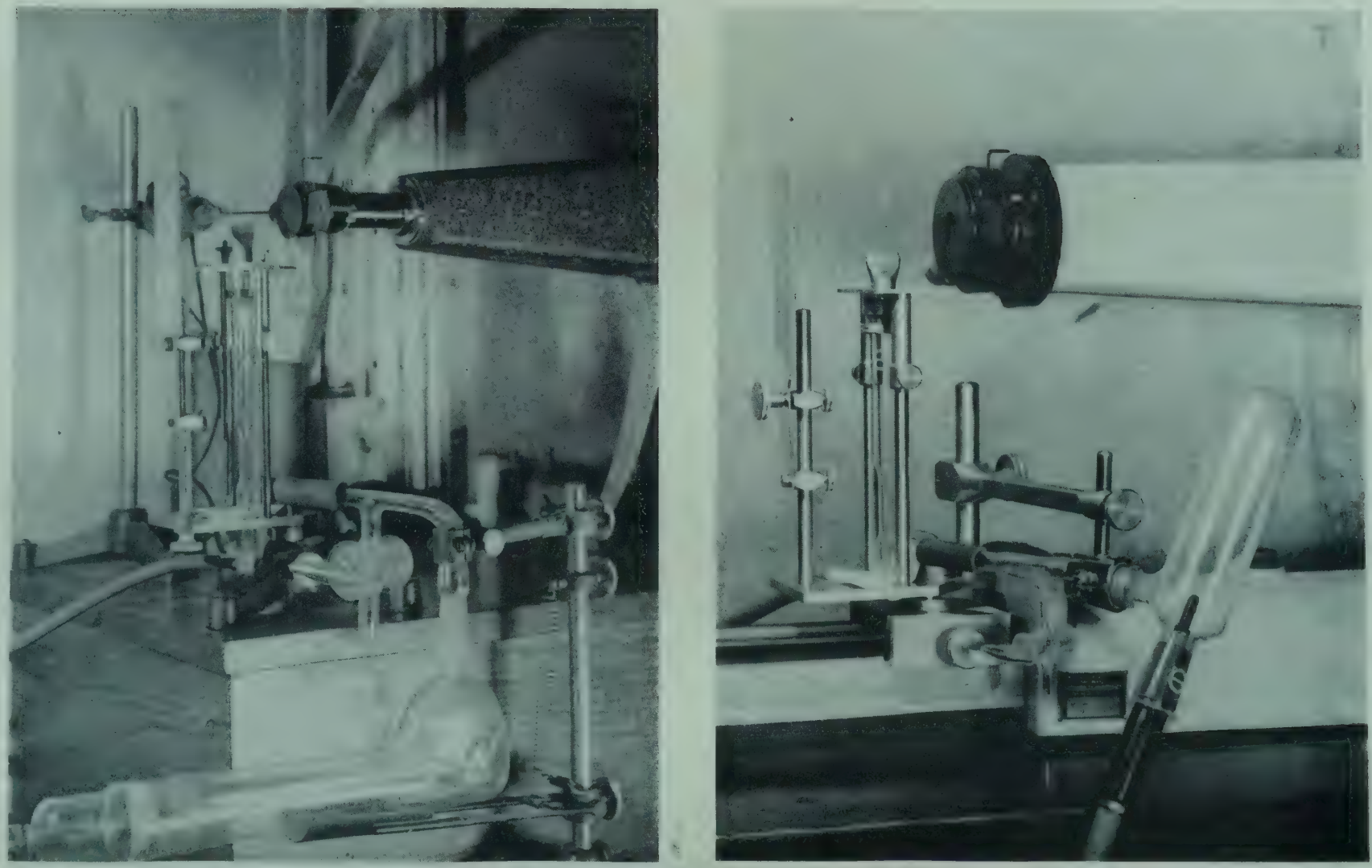

FIG. 15.—The Lundegårdh burner and atomizer: (a) earlier type and (b) current design. Both burners with the slit-type burner top

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Fortunately most of the analytically important flame lines occur in the region from 3200A to 5000A where interference from flame bands does not occur. The Mg line at 2852A lies in the 1,0 OH bands, but its determination is feasible as a band of equal intensity to that on which it falls lies near it and can be measured in the same way as the continuous background for other elements. The rather insensitive Zn lines at 3072.1 and 3075.9A lie in the strong 0,0 OH bands and can be seen only with a narrow slit. A typical flame spectrogram is illustrated in Fig. 14.

The general appearance of the Lundegårdh apparatus is illustrated in Figs. 15a and b which show the earlier and current designs of sprayers. There is little difference in the performance of the two designs, sensitivity and accuracy being about the same, but the more recent requires less solution, 2-10 ml. in place of 10-20 ml., and operates at a lower air pressure, although, of course, requiring the same volume of air for a flame of comparable size.

The production of spray occurs in the atomizer nozzle, which sucks up solution from the supply in the glass vessel and passes it, in the form of a fine spray, through the connecting tube into the burner where it is mixed with acetylene. The two types of sprayer are illustrated diagrammatically in Figs. 16a and b. In both instances the compressed air enters at A and on passing from the jet B through the disk E sucks up solution from the reservoir C through the aperture D. The spray formed passes through the chamber F into the sprayer vessel, where the larger drops are deposited on the walls. In both designs the distance between B and E is adjustable to obtain optimum efficiency for the air supply being used. The possible variables, which must be adjusted to their best values, are the air pressure (fixed to some extent by the volume of air needed to give a suitable flame), the size of jet B (directly related to the air pressure), the size of the aperture in E and the distance between B and E.

Only the finest droplets should reach the flame, so that the adjustment should ensure the production of the greatest possible quantity of fine spray. With fine droplets, the water evaporates in the flame before the zone of combustion is reached, so that the nucleus of salt is available for quick volatilization. The design of the sprayer vessel should be such that large droplets, if formed, are trapped on the walls and run back to the reservoir. If they are introduced into the flame they lead to irregularities, intensified in the earlier type burner by quick blocking of the platinum gauzes. In the earlier design the nozzle is entirely of platinum-iridium, apart from a short length of rubber tubing dipping into C. The newer model is of ebonite with the jet B and the disk E of platinum-iridium.

The air supply can be obtained from a cylinder of compressed air or from an air compressor through a reservoir held at about 10 atmospheres. Sufficient accuracy of control is obtained with the standard type of regulator (e.g., British Oxygen O.R.13.) The working pressure depends on the individual sprayer. The older model generally operates at 5-7 atmospheres

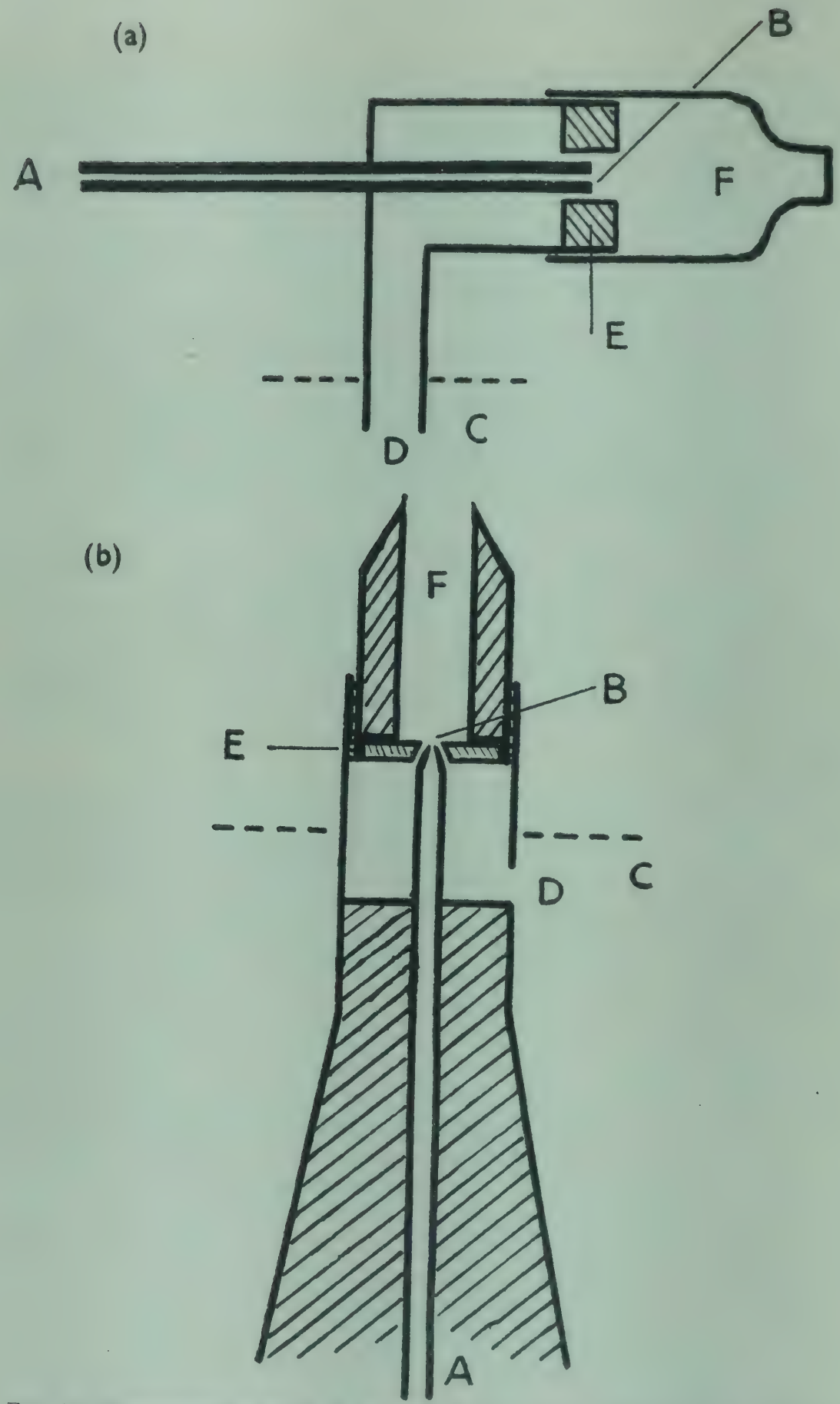

FIG. 16.—Diagrammatic sketch of atomizer nozzles for the Lundegårdh method: (a) horizontal and (b) vertical types

(Lundegårdh, 1934; Mitchell, 1936; Pallmann and Hasler, 1940) whilst pressures of 2-3 atmospheres (Lundegårdh, 1936), 2 atmospheres (Ells, 1941), and 2.8 atmospheres (Cholak and Hubbard, 1944 b) are reported for the newer design, although McClelland and Whalley (1941) use 7 atmospheres for the latter.

The smaller volume of solution which the newer model requires results from the shape of the atomizer vessel and the use of a vertical rather than a horizontal nozzle, assisted by the smaller wall area of the sprayer vessel. Manipulation is probably somewhat more convenient and the danger of breakage less. The advantage of the smaller volume in general routine analysis, where the solutions have to be subjected to previous chemical manipulation, is questionable. Filtration and adequate washing of filter papers to a volume of less than 50 ml. is an operation requiring considerable care, and at the Macaulay Institute it has been found more convenient to work to a 50 ml. volume than to 25 or 10 ml. when batches of 16 solutions are being done together, despite the extra materials and evaporation time required for the larger initial aliquots.

Acetylene enters at the base of the glass burner tube through a silver nozzle. The acetylene supply is obtained from a cylinder, and is controlled at a pressure of 20-40 cm. of water, depending on the size of the aperture in the nozzle. The flame size is the criterion of the amount of acetylene supplied, and this having been decided, the optimum amount of air necessary can be found by experiment. Generally air sufficient to give about 60% combustion of the acetylene is used, the remainder of the oxygen coming from the surrounding atmosphere, some 34 litres of acetylene and 257 litres of air being consumed per hour according to Lundegårdh (1936). Solodovnik and Gusyatzkaja (1940) give figures of the same order, namely, 0.6 litres of acetylene and 6.4 litres of air per minute. The acetylene pressure is standardized by means of a water manometer and adjusted by a pressure regulator. One is supplied for the purpose by the British Oxygen Company. The author's experience has been entirely of the Swedish Aga type (system Dahlen) which is very satisfactory. A means of stabilizing the gas pressure to a similar type of burner, using coal gas instead of acetylene, is described by Herrmann and Lederle (1942).

The burner tube is generally of Pyrex glass, with a metal top (plated brass), carrying a platinum-iridium tip. If the aperture is round (5.5 mm. diameter) a series of 8 interchangeable platinum gauzes is fitted about 10 mm. below the aperture on a disk which can be rotated to bring a new gauze into position as necessary. These gauzes, which serve to stabilize the flame and prevent striking back, are not necessary if the top has a slit type aperture (20 mm. × 1 mm.) as described by Lundegårdh and Philipson (1938). The longer axis is placed in the optical axis of the spectrograph, when used as a simple flame source. A plane mirror, chromium or rhodium plated, immediately behind the flame, reflects light back to the slit, and, according to Lundegårdh (1934), increases intensity by as much as 80-90%.

Lundegårdh (1941, 1945) has developed a completely automatic version of his apparatus in which solutions are carried to the sprayer vessel

on a conveyor belt, the filling and rinsing being carried out automatically, as is the exposure. The spectrograms on microfilm are developed, fixed and washed before passing through a recording microphotometer, from the record of which the results can be read off. The most complete description, with diagrams of the equipment, is given in Lundegårdh (1945), an English translation of which is in preparation.

Numerous workers have modified the original Lundegårdh atomizer. Most of these were attempts to reduce the volume of solution necessary, as although 25 ml. is generally available for analysis of soils and plant materials, other applications, such as determinations of alkalis in blood serum, required a determination on a smaller volume. The earliest reported vertical type, using only 2 ml. of solution, appears to be that of Jansen, Heyes and Richter (1934 b), but the high concentrations and long exposure times suggest that the design was inefficient. It resembled that of Gouy (1879) in that the solution was drawn up through a central tube with the compressed air in the outer tube. An air pressure of less than one atmosphere above atmospheric was employed. Waibel (1935) produced two vertical atomizers working with small volumes. One was all-glass, whilst the other had a metal nozzle, and both appear from the data available to be similar in efficiency to the Lundegårdh design. The small sprayer vessel employed is very similar to that of Lundegårdh but with the outlet nearer the top. Waibel's apparatus has been widely used in Germany in the Siemens equipment for the direct photometric determination of potassium.

Jansen, Heyes and Richter (1934 b) experimented also with the slit-type burner, suggested to them by work of Locher (1928), but found water and other bands from the combustion of the acetylene too dark. Waibel (1935) recommended a slit type burner top for lines which did not show reversal.

Lundegårdh (1929) reported that 0.037 g. of solution was brought into the flame per minute by his first, less efficient, sprayer compared with 0.02 g. for Klemperer's electrolytic atomizer, whilst Waibel (1935) used 0.05 ml. per minute in his type, a figure which compares with Putzmann's (1940) value for the same type, of 0.07 ml., calculated from the loss in weight over 10 minutes. Cholak and Hubbard (1944 b) found a larger weight of spray, namely 0.15 g. per minute, carried into the flame with their atomizer which they built themselves following Lundegårdh's design. Schuffelen (1940) gives figures for different atomizer settings and for mg. of solution per litre of air at different air pressures.

It is highly desirable that those using an apparatus of the Lundegårdh type should undertake its initial adjustment, in order to gain insight into the effects of change in the different variable factors. After this initial adjustment has been carried out and suitably stabilized supplies of air and acetylene provided, the use of the equipment becomes a matter of routine, and it can be put into the hands of laboratory assistants after a very short training. There must of course be adequate supervision with occasional checks on known solutions.

The procedure with the standard Lundegårdh equipment is as follows :

The acetylene and air pressures are adjusted to the predetermined most suitable values, the flame having been lighted, with acetylene alone passing, a few seconds after the acetylene is turned on. The position of the flame is then checked for height and alignment, with air passing through an empty sprayer vessel. Alignment is checked by observing the image of slit and flame in the mirror behind the flame, from a point above the prism of the spectrograph, or between it and the slit. Distilled water is put into the sprayer vessel and the appearance of the flame checked to make sure that the sprayer is working properly. The sprayer vessel is rinsed thoroughly with 10-15 ml. of the solution to be used, which is then replaced by 5-20 ml. of the same solution. After the spray has passed through the burner for 15-30 seconds, to allow of equilibrium conditions being established, the spectrograph slit shutter is opened and the exposure commenced. This is generally of 60 seconds duration but depends on the solution, spectrograph and plate being employed. After the exposure is completed, a duplicate spectrogram of the same solution is taken adjoining the first by moving the plate the necessary distance and making a second 60 second exposure. The solution is now poured out of the sprayer vessel which is rinsed thoroughly by the next solution to be analysed, the procedure then continuing as above. It has been found that the method of rinsing with the following solution is quite satisfactory for work with series of soil or plant material extracts where composition varies little from sample to sample. The dilution effect of distilled water rinsing is thus avoided : to overcome it much more complete washing out with the following solution is required. When one solution is seen subsequently to have a content abnormally different from those adjoining it, that sample (diluted) and the one following should be repeated. As this seldom occurs in soil work, the saving of time by the process adopted is appreciable and no loss of accuracy has been found.

The spectrograph employed for the Lundegårdh method should be of medium dispersion (spectrum length 2000-8000A 12-25 cm.), as the number of lines obtained even for line-rich elements such as iron is not great, but on the other hand the dispersion provided by the smallest instruments (spectrum length 2000-8000A less than 12 cm.) is not adequate. Lundegårdh (1934) recommends a dispersion of 150A per mm. at 4000A. Oertel and Stace (1946) found a large quartz spectrograph to be rather unsatisfactory for flame work.

The author has employed the Hilger Medium Quartz Spectrograph, and this size is very convenient. As flame spectrograms do not generally extend below 2800A it is unnecessary to employ the full 10″ × 4″ plate. A 5″ × 4″ plate in the long wavelength half of the plate holder is adequate. As the flame is situated immediately in front of the slit, only 5 cm. from it, it is desirable to have the slit shielded by a plane quartz window, to protect it from corrosive fumes. The slit is reduced in length to about 1.5 mm. to

enable a sufficient number of spectrograms, in duplicate, to be carried on one plate. It is possible to obtain 44 spectrograms, 2 mm. apart, on the 4″ wide plate of the Hilger E316 Medium Spectrograph. The slit width is considerably wider than usual in spectrographic analysis, about 0.04 mm., as this gives a satisfactory background density and does not resolve the K doublet at 4044/47A or the Mn triplet at 4031/34A. When a spectrograph with too small a dispersion is employed, these K and Mn groups are not adequately separated, and mutual interference may occur.

As the shutters fitted to most spectrographs are quite inconvenient, another must be provided in front of the slit to allow accurate exposures to be made. The best type is operated by means of a solenoid and controlled either by a button switch and stop watch, or a clockwork or electric switch giving an on-period of suitable duration.

The laboratory in which the equipment is set up should be provided with a hood with a slight suction, immediately over the flame. This helps to stabilize the flame and allows some movement in the laboratory whilst exposures are in process, although this should be kept to a minimum. It also helps to keep the laboratory temperature uniform and the atmosphere clean, as appreciable amounts of the cations being determined are sprayed into it.

The most sensitive lines quoted by Lundegårdh (1934) for 34 elements are given in Table 1. For several elements, such as Rh, numerous wavelengths were given without indication of sensitivity.

TABLE 1

Wavelength and Sensitivity of Lines visible in the air-acetylene Flame, from Lundegårdh (1934)

Element	Wavelength	Lower limit of sensitivity	Element	Wavelength	Lower limit of sensitivity
Ag	3280.7	0.000005M	Li	6707.9	0.000001M
Au	2676.0	0.0001M	Mg	2852.1	0.0002M
Ba	5535.5	0.001M	Mn	4030.8	0.000005M
Ca	4226.7	0.00001M	Na	3302.3/02.9	0.0005M
Cd	3261.1	0.002M	Nd	4634.2	—
Co	3526.9	0.0002M	Ni	3414.8	0.0002M
Cr	3578.7	0.0001M	Pb	4057.8	0.0006M
Cs	4555.3	0.0005M	Pd	3634.7	0.0002M
Cu	3247.5	0.000005M	Pr	5623.0	—
Dy	4527.7	—	Rb	4201.8	0.0001M
Fe	3859.9	0.0001M	Rh	3323.1	—
Ga	4033.0	—	Ru	3725.9/28.0	0.0001M
Gd	4614.5	—	Sc	4670.4	—
Hg	2536.5	0.001M	Sr	4607.3	0.000002M
In	4101.8	—	Tl	3775.7	0.000002M
K	4044.2/47.2	0.0002M	Y	4643.7	—
La	4383.5	—	Zn	3072.1	0.5M

For the analysis of agricultural materials a composite standard solution, containing Ca, Sr, Mg, K, Na, Mn and Fe is employed. Li can be included, but this requires the use of red sensitive plates, such as Ilford Soft Gradation Panchromatic, or Long Range Spectrum. For normal work Ilford Zenith plates are suitable, requiring a 60 second exposure time with a Hilger Medium Quartz Spectrograph. Development is $5\frac{1}{2}$ minutes at 18°C. in Ilford I.D.2 metol-hydroquinone developer. These plates cover the 2800-5000A spectral region in which the lines of all the above elements other than Li occur. The wavelengths employed are those quoted in Table 1.

The most concentrated standard solution should contain (Mitchell, 1936) the following molar concentrations of the chlorides of the elements :

Ca	M/4000	K	M/200	Fe	M/200
Sr	M/10000	Na	M/100	Mn	M/4000
Mg	M/200	Li	M/4000		

The solution should be in dilute hydrochloric acid of about N/20 to prevent hydrolysis of iron and manganese. Five dilutions of this standard solution, of one-half, one-quarter, three-twentieths, one-tenth and one-twentieth, provide a convenient dilution series, giving densities suitable for measurement and covering a twenty-fold concentration range for each element. Standard solutions of similar composition are recommended by Ells and Marshall (1939) and Pallmann and Hasler (1940). Corresponding analytical ranges quoted by Cholak and Hubbard (1944 b) are

Ca	0.5 — 20 mg./l.	K	6.0 — 400 mg./l.	Fe	5.0 — 500 mg./l.
Sr	0.4 — 30 mg./l.	Na	30 — 2500 mg./l.	Mn	0.5 — 30 mg./l.
Mg	5.0 — 500 mg./l.,				

the lower values being obtained only by increased exposure time.

In routine analytical determinations, duplicate spectrograms of 6 standard solutions are carried on the same plate as duplicate spectrograms of 16 solutions for analysis. Photometry of the Lundegårdh plate is simpler than that required for most other methods, because of the reproducibility of the source and because standards can be carried on each plate. The method employed, as already briefly noted (Lundegårdh, 1934), is to read galvanometer deflexions for the line and the background on which it is superimposed and to take the ratio of the values obtained, the galvanometer being adjusted to give a total blackness reading of zero. A clear plate reading is not required, nor need the galvanometer sensitivity be standardized : any slow drift which does not affect the results over the period of a few seconds required to measure a line and its background can be disregarded. For Ca, Sr, K, Na, Mn and Fe the choice of a point adjoining the line at which to read the background is straightforward, as it is only infrequently that a clear point in the neighbourhood of the line cannot be found, e.g., for K in the presence of Mn and Pb, when a point beyond the Pb line at 4057A has to be taken. Mg, on the other hand, lies in a banded background on a band of intensity equal to that which occurs immediately below it in wavelength, so that for this element one reads the Mg line and

the first band of shorter wavelength, treating this as background. With spectrographs of smaller dispersion than Hilger Medium, some difficulty may be found in reading the background for Fe 3859.9A, but this can be overcome by reading the minimum background between it and the next longer Fe line. For Li 6707.9A there is no appreciable flame background and an internal standard has to be employed for accurate results. Lundegårdh (1934) has described a microphotometer employing a Kipp Vacuum Thermoelement as the sensitive element, the ribbon serving to scan the plate and eliminating the necessity for a slit. A projection lens behind the thermoelement gives an enlarged image showing the position of the spectrogram relative to the ribbon. Any standard type of microphotometer may however be employed.

The ratio of line plus background to background deflexion gives the transmission of the line free from background, and this value plotted against concentration for the standard solution spectrograms gives a working curve from which concentration values for the unknown solutions can be obtained. A series of typical curves is illustrated in Fig. 17. These curves are logarithmic in form, but Lundegårdh (1938a) and Cholak and Hubbard (1944b) have pointed out that over the lower concentration ranges the use of the logarithm of the line to background ratio gives a straight line. Greater

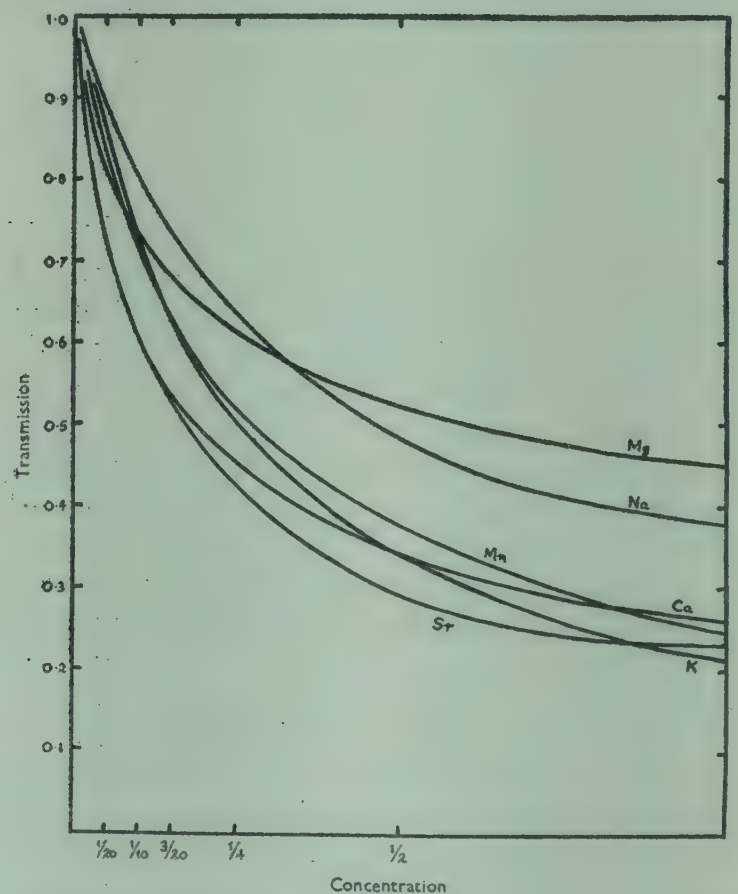

FIG. 17.—Typical Lundegårdh working curves of the ratio of the galvanometer deflexions of line plus background to background plotted against concentration

accuracy than the standard deviation which is usually obtained of ±5% or better is possible if an internal standard whose behaviour in the flame is similar to that of the element being determined is introduced into the solution (Lundegårdh, 1934; Cholak and Hubbard, 1944 b), or simply by replication of the spectrograms.

Results by Cholak and Hubbard (1944 b) using Co as an internal standard for the above elements show standard deviations, with duplicate spectrograms: Mg ± 7.6%, Na ± 1.8%, Fe ± 2.3%, Mn ± 2.1%, K ± 1.55%, Ca ± 3.6%, Sr ± 1.8%. The lower accuracy for Mg is found by most workers, and is due to the rather flat calibration curve obtained with the Mg 2852A line. Oertel and Stace (1946) report that even with an elementary technique, an average standard error of less than 4% was obtained. Burström (1935) had sugar beet juice analysed chemically for Na, K, Ca and Mg at three different institutions, and compared the results with his determinations by the Lundegårdh method. The agreement between the spectrographic and chemical methods was as good as or better than that between the different laboratories employing the usual chemical methods.

In addition to the elements noted above, adequate sensitivity for certain purposes can be obtained for Cu, Pb, Ag, Co, Ni, Cr, Rb, Cs and even Ga (Rusanov, Kunina and Vasilev, 1937) and Tl (Solodovnik and Gusyatzkaja, 1940). Suitable concentrations for standard solutions of chlorides or nitrates of these elements employing the wavelengths given in Table 1 are:

Cu	M/1000—M/20,000	Cr	M/100 —M/2000
Pb	M/200 —M/4000	Rb	M/1000—M/20,000
Ag	M/4000—M/80,000	Cs	M/1000—M/20,000
Co	M/200 —M/4000	Ga	0.006—0.4%
Ni	M/200 —M/4000	Tl	0.003—0.3%

The Ga and Tl data are quoted from the above authors.

For Rb and Cs much greater sensitivity can be obtained by choice of suitable plates from the range of Kodak plates for scientific purposes, using the Rb 7800.2A and Cs 8521.1A lines. For Na greater sensitivity, depending on the plate chosen, is obtainable from the 5890/6A doublet, whilst for K the line at 7664.9A is very sensitive, M/50,000—M/1,000,000 being a suitable range with Kodak N.I plates. As the flame background is absent above 5000A, the normal method of photometry is not available and an internal standard is desirable. The author, in unpublished work, has used Li 6707.9A (M/10,000) as internal standard for K. The greatest difficulty experienced has been the avoidance of K contamination when working at such low concentrations. The use of the near infra-red has also been studied by Gazzi (1934, 1939), who has modified the Lundegårdh technique somewhat

by incorporating a concave mirror and a rotating sector. Gazzi quotes the following wavelengths and useful ranges, using Agfa infra-red plates :

	λ	mg./ml.	
Cs	8521	0.10 —2.0	Agfa 850
Rb	7800	0.02 —0.40	Afga 800
	7947	0.025—0.40	,,
K	7665	0.01 —0.20	,,
	7699	0.012—0.20	,,
Li	6708	0.005—0.04	Agfa Spectral Total

Errors in the results obtained by the Lundegårdh method can be caused by variation in the flame conditions between unknowns and standards, or by certain differences between the composition of the unknown and the standard. As typical of the effect of air and acetylene pressure variation may be taken the results of Cholak and Hubbard (1944 b) who found that, for an acetylene pressure of 25 cm. and air pressures between 25 and 55 lb. per sq. in., Ca and Sr intensities were constant to 35 lb. and then decreased, whilst Na, Mn, Co, Fe, K, Cu and Mg increased with pressures up to 40 lb., then remained constant. For a lower acetylene pressure, the effects were similar but occurred at lower air pressures. Similar results have been reported by Pallmann and Hasler (1940), Lundegårdh (1934), Ells (1941), Giesecke, Rathje and Krummel (1938), Putzmann (1940) and Lohse (1935). These results must be considered in the light of Lundegårdh's (1936) work on the relative intensities of the different elements at various distances above the blue cone of the acetylene flame, as variations in the air-acetylene ratio may merely change the optimum region of the flame for different elements. Lundegårdh (1936) found that whilst Ca and Sr were strongest just above the tip of the blue cone, optimum K emission occurred about one centimetre higher. Thus the air and acetylene pressures chosen, and the point in the flame which is opposite the slit must be the compromise which best suits the determination being made. Schuffelen (1940) has given data for the effect on flame size of different solutions, and for small changes of air and acetylene pressures from normal. Generally, changes of these pressures, within the limits of control by a water manometer for acetylene and a mechanical pressure gauge for air, do not have a significant effect on the results obtained.

Errors may also arise from variation in the composition of the solution between unknowns and standards, either because of differences in the amount sprayed into the flame, or because of interference effects in the flame.

Putzmann (1940) has studied the actual amounts of solution carried as spray to the burner when viscosity and density vary. Change in viscosity had no significant effect on the amount of solution atomized, but the volume sprayed varied with the density of the solution, although the weight was constant within experimental error. Putzmann found also that the volume sprayed increased with rise in temperature, so that standards and unknowns should be at the same temperature, as pointed out earlier by Lundegårdh (1934). Schuffelen (1940) related the change in weight sprayed at different temperatures to the viscosity. As determinations are made on a concen-

tration basis it is the volume sprayed, not the weight, which is the critical value, but as far as temperature changes are concerned, the density changes are negligible, so that this difference can be ruled out in this instance. Pallmann and Hasler (1940), adding glycerine up to 20% with viscosities of 0.0102 to 0.0183 (densities 1.000 to 1.047), found depressions of K of up to 3.8% which is probably within experimental error, but can be accounted for by change in density. The same workers considered also the possible influence of surface tension, but no conclusive effect was observed. Schuffelen (1940) draws attention to the temperature changes which occur in the solution as a result of spraying, and gives figures for the effect of concentration change due to the evaporation of the solvent during spraying. The effect is negligible for periods of up to 5 minutes, but the sprayer should not be left operating unnecessarily for a long period before a determination is made.

A photoelectric device for controlling the amount of spray passing into the flame has been suggested by Mavrodineanu (1940), whilst a further source of possible trouble, encrustation of salt by evaporation of spray on the acetylene jet, thereby reducing the acetylene flow, can, it is reported by McClelland and Whalley (1941), be avoided by wetting the acetylene.

Changes in the composition of the solution, besides affecting the viscosity or density, may cause errors in determinations as a result of interference effects of another element or compound on the element being determined. Some decrease in K intensity occurs when the HCl concentration in the solution exceeds N/10 (Lundegårdh, 1936; Ells, 1941; Schuffelen, 1940). Other acids do not appear to produce this effect. Unpublished work of the author shows a general tendency for a slight depression to occur with most elements in the presence of high contents (M/10 or higher) of many neutral salts, other than ammonium salts. Fe is generally low in acetate solutions, probably because of the formation of a basic acetate. The general rule to avoid such effects is to add an equivalent amount of the interfering substance to the standard solutions. It would appear from the results so far available that samples containing high contents of extraneous salts are more susceptible to variation than are solutions which are not so loaded, although the author's experience has not been so unsatisfactory as that of Schuffelen (1940) in this respect.

The most serious interference effect so far reported is that of Al on Ca and Sr (Mitchell and Robertson, 1936). An Al content of M/2500 reduced Ca and Sr results to about one half of the correct value. A similar effect has been noted by Pallmann and Hasler (1940), Schuffelen (1940) and others. Correct results for one of the cations can be obtained by adding an excess of the other (Mitchell and Robertson, 1936), but the effect must always be kept in mind particularly with acid extracts of soils. Lundegårdh (1941) has used the effect to reduce the sensitivity of Ca in solution and so to determine it in the same spectrogram as other elements.

Huldt (1944) found that Ca in concentrations up to M/10 depressed the Sr II 4078A line between M/10,000 and M/100 to as little as one twentieth of its proper value, but that the Sr I 4607A line was enhanced at M/50,000 to

almost double its value, falling to the normal content at M/5000, thereafter producing a slight depression. This effect, and also the effect of Al on Ca, was studied further by Huldt (1946), the latter being apparently due to the formation of a Ca-Al compound, but no molecular spectrum of a newly formed molecule could be observed (*cf.* Mandelstam, 1939 b).

The interference effects can be grouped roughly into four categories.

(a) Coincidences such as the enhancement of the Mg 2852.1A line by Na 2852.8A at high Na contents, or K 4044/4047A by Fe 4045.8A at high Fe contents. These can be disregarded at concentrations of Na below M/25 or Fe below M/100.

(b) Effects due to background enhancement, such as occurs with high concentrations of Mg or Na. This is to a great extent compensated by the usual method of photometry and very appreciable changes in background can occur without error in the results.

(c) Specific interferences such as that of Al on Ca and Sr. Such effects are possibly due to the production of compounds which are not broken down at the temperature of the flame.

(d) General reductions of intensity as a result of the presence of substances which affect the solution or flame properties.

These effects have been studied, in so far as they affected their specific problem, by most of the workers who have used this method. An interesting example of an intensity reduction by an organic compound, previously unreported, is that of chloroform on Ca and Sr. The addition of a few drops of $CHCl_3$ to stop mould growth in solutions caused a very great depression of the Ca and Sr lines until the volatile $CHCl_3$ was removed from the solution in the air stream.

Applications of the Lundegårdh technique and its modifications to different problems have been described by numerous investigators. Jansen and Heyes (1932, 1934) and Jansen, Heyes and Richter (1934 a, b) determined alkalis and alkaline earths in spring and mineral waters and in blood serum. Norinder (1938, 1939, 1942) has applied it to the determination of Ca, K, Na, Mg and Fe in blood. Mineral waters were also studied by Intonti (1939) and Gazzi (1934, 1939). Tsuge (1933) determined K in ashes of rice straw and Sr and Li in extracts of Manchurian alkaline soils. Griggs (1939, 1945) and Griggs, Johnstin and Elledge (1941) have used the Lundegårdh technique for the determination of Cu, Fe and Mn in orange juice and for the analysis of other biological materials, whilst Ambler and Griggs (1941) report analysis of Co and Ni in pectinates of these metals, finding good agreement with colorimetric results. Giesecke, Rathje and Krummel (1938) applied a modified Lundegårdh method to the determination of K in the ashes of plants grown by the Neubauer method.

A modification of the Lundegårdh method by some Russian workers has been the use of a very finely ground powder instead of a solution. Rusanov (1933) determined the alkali metals in minerals such as mica, whilst Ivanov (1939) reports the determination of Cu in soils.

Methods of preliminary extraction of soils suitable for the application of the Lundegårdh method to the determination of exchangeable cations,

or of the easily soluble constituents, have been described by Mitchell (1936, 1939) and Ells and Marshall (1939).

At the Macaulay Institute the normal procedure for the determination of exchangeable cations is to leach 20 g. of soil to 1000 ml. with neutral, normal ammonium acetate. An aliquot of 25 ml. is diluted to 100 ml. (including 10 ml. of M/100 $SrCl_2$) for the determination of Ca, whilst 900 ml. is evaporated to dryness on the water bath, treated with H_2O_2 to remove organic matter, and taken up in sufficient HCl solution to give a final concentration of about N/20 in 50 ml. after filtration. In this solution it is possible to determine K, Na, Mg, Sr and Mn, as it is only exceptionally that all do not fall within the concentration ranges of the standard solutions described above.

For soil advisory purposes an extract prepared by shaking 20 g. of soil with 800 ml. of 2.5% acetic acid for 2 hours is often employed. An aliquot of 600-700 ml. treated as described above gives a 50 ml. solution in which K, Mg, Na and Mn can be determined, whilst a 10 or 25 ml. aliquot is satisfactory for Ca. The addition of Sr is necessary in this instance to overcome any Al effect, although this is seldom encountered in the ammonium acetate extractions. It is preferable to follow the same procedure in both cases, so that the same standard solutions can be employed.

Ells and Marshall (1939) have preferred to leach 5 g. of soil to 250 ml., taking 200 ml. to 25 ml. for the actual determination. With these quantities, previous grinding to a fine powder was found to be necessary in order to obtain a representative sample.

For the determination of the cations extracted from the ash of plant materials by hydrochloric acid, 10 g. of oven dry finely ground material are ashed overnight at about 450°C., then taken to dryness twice with concentrated HCl on a steam bath, and taken up in 25 ml. of 2N HCl, filtered and diluted to 500 ml. This solution is suitable for the determination of Mg, Mn and Na, whilst a five times dilution is necessary for K. Still further dilution is required for Ca. These quantities are suitable for most types of plant material, but for some, e.g. turnips, with higher K contents, 2.5 g., taken to 250 ml. and diluted 10 times, is adequate. Several workers, for instance Cholak and Hubbard (1944 b), have preferred wet ashing rather than dry ashing for biological materials, as they found some slight loss of cations in the residue after dry ashing by their methods.

c. The Ramage Flame Emission Method

Ramage (1929) has described a method which gives the same type of spectrogram as the Lundegårdh method, by the introduction of the substance being examined into an oxy-coal gas flame by hand on a spill of pure filter paper. The Ramage burner comprised a wide (2 cm.) outer silica tube through which the coal gas was introduced, and a narrow central silica tube with a slit-shaped aperture, at the same level as the outer tube, which carried the oxygen. This type of flame, using coal gas-oxygen or occasionally

acetylene-oxygen mixtures, is hotter than the air-acetylene flame, and Ramage (1929) reported the detection of all the alkalis, Cu, Ag, Mg, Ca, Sr, Ba, Ga, In, Tl, Pb, Cr, Mn, Fe, Co, Ni, Pd, Ru, Rh, P, Bi and Ir and, in larger quantities, Au, Be, Zn, Cd, B, Al, Y, Sn, As, Sb, S, Se and Te. Most of the latter are much too insensitive to be of practical use. In a private communication Ramage gave, as suitable concentrations to be applied in fractions of a millilitre to the filter paper spill, the following percentage contents : Na 0.15, K 0.30, Ca 0.02, Li 0.0004, Rb 0.004, Mg 0.05, Cu 0.005, Mn 0.002, Fe 0.05, Ni 0.002, Co 0.005, Cd 0.10, Ag 0.0025, Sr 0.002, Pb 0.05 and P 0.4. Solids such as plant materials were examined by burning 0.05 g. of the dried material rolled in filter paper, whilst solutions were added to the filter paper by pipette.

Evaluation of the spectrograms was by inspection and visual comparison with standards, so that the results were qualitative or semi-quantitative. As the introduction of the spill into the flame was made by hand, both the point of introduction and the speed of introduction were subject to variation. As changes in the point at which the flame is examined cause appreciable differences in the results obtained in the Lundegårdh method, where the material is dispersed generally through the body of the flame by the air supply, this must be even more critical when the material can be introduced at a point which is variable as regards position and also distance into the flame, this varying with speed of introduction. Very considerable practice is thus required in the Ramage technique before any form of quantitative assessment can be carried out. The method has been applied by Ramage (1930) to the detection of Ag in mushrooms and to the analysis of various other biological materials (Ramage and Sheldon, 1931 ; Sheldon and Ramage, 1931; Ramage, Sheldon and Sheldon, 1933; Ramage, 1936 a, b). The high Ba content of Brazil nuts reported by Seaber (1933) was confirmed and found to be concentrated in the dark brown coat of the endosperm. Fox and Ramage (1931) carried out semi-quantitative analyses of organs and whole animals of annelides, molluscs and other invertebrates, finding Cu to be a universal constituent of all species analysed, and adding F to the above list of elements detectable in the flame, it being observed by the CaF bands. Whitehouse and Ramage (1933) determined Li in an attempt to measure the permeability of the skin to electrolytes.

Very considerable errors may have arisen in Ramage's work because of the uncertainty of the point of introduction and because of the comparison of biological materials (often burnt as dry matter without ashing) with standards added as pure solutions. His work is however worthy of notice because it comprises some of the earliest systematic applications of spectrographic analysis to biological problems, and because his method can be adopted with the minimum of equipment.

The obvious development of standardizing the introduction of the spill into the flame has been studied by various workers. Steward and Harrison (1939) and Kent (1940) employed mechanical feed devices which fixed the point of introduction within the limits of rigidity of the filter paper

spill, but left its speed of introduction to the personal judgement of the operator. Steward and Harrison (1939) give full details of the method of preparation of spills, working only with solutions. The method of photometry involved the use of the difference of line and background galvanometer deflexions, with the background deflexion adjusted always to a constant value. They were determining the uptake of Rb by potato tuber disks from solutions containing it, and the amount available for determination did not necessitate a high sensitivity. Standard spills of Munktell's Swedish No. 00 filter paper 3″ × 0.7″, rolled into a spiral, carried 0.1 ml. of standard Rb solutions containing 2-13 mg. equivalents of Rb per litre. Analysis solutions were diluted to within the same range. The Rb lines at 4215.6A and 4201.8A were employed. The error of the mean of replicate determinations of Rb in potato tissue extracts need not exceed ±5%, with Ilford Process plates.

Kent (1940) used a solution of plant ash in nitric acid on filter paper spills which were fed into a Ramage type flame by means of a manually operated feeder at about 2″ per 10 seconds. The useful working range was between 0.4 and 4.0 μg. of Li on the spill, using Ilford Rapid Process Panchromatic plates for the Li red line at 6708A. Li contents of plants grown in normal and lithium treated soils were determined.

Roach (1946) has described a modification of the Ramage technique employing an ordinary commercial oxy-acetylene lead-burning blowpipe, with the top of the nozzle replaced by a platinum plate about 1 mm. thick with a hole 0.02″ in diameter. The oxygen pressure is 28 ± 1 cm. and the acetylene pressure 0.1 cm. mercury. The spill of Whatman 541 filter paper, 10.2 cm. × 1.6 cm., is folded and charged with 25 mg. of dried, ground plant material in two ingenious pieces of apparatus made of wood that avoid finger contamination of the paper, as well as ensuring the production of reproducible spills. The spill is then carbonized in NH_4Cl vapour at 350°C. (Roach, 1939). This has a twofold purpose : it converts some of the inorganic salts to chlorides as well as removing the bulk of the organic constituents of the plant material. The paper is completely charred and burns smoothly on being fed into the flame. The spill is placed in a platinum holder, being held in position by a spring and propelled along a trough into the flame by a wooden pusher driven by a synchronous motor. The flame, 40 cm. long and quite narrow, is protected from draughts by a metal chimney. The spill is fed in at constant speed about 0.5 cm. above the nozzle (i.e. just above the central cone) whilst the optical axis of the spectrograph is 2 cm. above the nozzle and 1 cm. above the top of the spill. The nozzle is about 17 cm. from the slit, no condensing lens being used. A constant length of each spill (three-quarters) is burnt. A plane mirror behind the flame reflects light back to the spectrograph.

It seems possible (Roach, 1940) that when the carbonized spill technique with solid material is employed, the nature of the anion is of some importance, and the work of Török (1940) may be mentioned here, as he found visual sulphate and phosphate effects in some alkaline earth elements with spray introduction into a horizontal bunsen flame.

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The Ca line indicated by Roach (1946) at 4225A is an error due, according to Lundegårdh (1934), to Löwe, who reported it in the first edition of his Atlas. It is to be found also in the wavelength tables of Lundegårdh (1929), Twyman and Smith (1931) and Löwe (1936), but not in those of Harrison (1939 a) or Kayser and Ritschl (1939).

Mitchell (1941) has compared a modification of the Ramage technique, using the Steward and Harrison mechanical feed device and the standard Ramage burner, with the Lundegårdh method, as regards sensitivity and accuracy. Ilford Zenith plates were used up to 5000A and Long Range Spectrum plates above that wavelength. Data for sensitivity, using 0.05 ml. of solution on the spill were :

Element	Wave-length	Concentration range	Element	Wave-length	Concentration range
Li	6707.8	M/5000 —M/100,000	Sr	4607.3	M/500 —M/10,000
Na	3302.3	M/100 —M/2000	Fe	3859.9	M/100 —M/2000
K	4044.1	M/200 —M/4000	Co	3529.8	M/100 —M/2000
Rb	4201.9	M/1000 —M/20,000	Ni	3414.8	M/100 —M/2000
Rb	7800.2	M/10,000—M/200,000	Cr	4254.3	M/50 —M/1000
Cs	4555.4	M/1000 —M/20,000	Mn	4030.8	M/2000—M/40,000
Cs	8521.1	M/2000 —M/40,000	Cu	3247.5	M/2000—M/40,000
Mg	2852.1	M/100 —M/2000	Pb	4057.8	M/100 —M/2000
Ca	4226.7	M/500 —M/10,000	Ba	Only diffuse bands	

The relative sensitivities of the two methods are roughly the same when the amount of solution introduced on the spill, 0.05 ml., is of the same order as the amount of spray introduced into the Lundegårdh flame (see p. 40).

As a measure of the relative accuracies, determinations made with Mn showed that the standard error of the mean of duplicates by the Lundegårdh method was $\pm 4.5\%$, whilst that of quadruplicates by the modified Ramage method was $\pm 6.1\%$. This difference in favour of the Lundegårdh technique is almost certainly due to the greater difficulty of obtaining reproducible introduction of the sample into the flame in the Ramage method. It is possible, as Steward and Harrison (1939) have shown, to improve the accuracy with practice, but the author's preference is for the more easily standardized Lundegårdh technique.

A method similar to that of Ramage has been used by Borovick-Romanova (1938, 1944 a) for the determination of Rb in sea water. A paper spill was fed into an acetone vapour burner supplied from a special carburettor. Interference effects due to the presence of Na and Li salts are reported. Bossuet (1932, 1933, 1935) has determined the alkali metals present in mineral waters in an oxy-acetylene flame by their introduction on a splinter of magnesium pyrophosphate. Gatterer (1942) has suggested as a spectral source the use of the flame which surrounds a carbon rod heated to high temperature by passing a high current through it. Increased sensitivity of certain lines and bands is thereby obtained, but there are difficulties in the way of accurate quantitative applications.

Chapter 5

ARC METHODS OF SPECTROGRAPHIC ANALYSIS

I. THE NORMAL DIRECT CURRENT ARC

a. General

The energy of the flame source is too low to give satisfactory excitation of many elements, and even those which can be excited can in general only be determined in quantities above the normal trace amounts present in biological materials. Thus it is necessary to turn to one of the electrical means of excitation, and of these the direct current arc is the simplest. This is the most generally employed source for the analysis of non-conducting samples such as are encountered in biological work, and consists of a continuous discharge of direct current at a relatively low voltage and high current density over the gap between two conductors. The sample can be placed in a depression in one of the electrodes; the high temperature produced by the arc brings about the volatilization of the sample and so introduces it into the arc column where emission takes place.

The electric arc discharge was first observed and described by Sir Humphrey Davy (1802), using the large battery at the Royal Institution as the source of current. He formed arcs with various metals and with carbon electrodes, and noticed with the latter that the hottest part was in the anode crater on the positive electrode. The name *arc* was applied because of the shape assumed by a horizontal discharge, resulting from the upward movement of the heated air. The arc was first employed for spectroscopic analysis by Bunsen in 1844 (Kayser, 1900). A typical d.c. arc runs off a 200-250 volt supply at 5-10 amp. with a voltage drop of 40-80 volts over the arc gap of 1-10 mm. This entails a supply either from direct current mains or from alternating current mains by rectification with a rotary convertor or a valve or metal rectifier. It is desirable to have at least 12-16 amp. available. A resistance, capable of adjustment whilst the arc is running, is required to control the arc current, which is registered on an ammeter. Only two of the three variables, current, voltage and arc length, are independent, and all are related to the conductivity of the arc gap, that is, to the nature of the sample and electrodes. With some circuits an inductance may be of service in controlling fluctuations of the applied voltage, which may be of the order of 50%. This is used chiefly in the United States where low voltage supplies of about 110 volts are commonly employed. The direct current arc is not self igniting and the arc is made

either by bringing the electrodes into contact, then separating them to the proper distance ; by touching both with a conducting material, preferably similar in composition to the electrodes ; or by applying a high frequency high voltage carrier current. Much qualitative and semi-quantitative work has been done by filling a small quantity, up to 50 mg., of material into a wide shallow boring in an electrode of carbon or copper and striking an arc to an unfilled electrode of the same material, increasing the current up to 5 to 15 amp. after the arc has been struck. It is usually desirable to strike the arc at a low current, with high ballast resistance in circuit, and then to increase the current steadily at a rate governed by the behaviour of the arc itself. Loss of powdered material by spluttering is thereby reduced, although there is at the same time the possibility of some decrease in reproducibility of the more volatile constituents of the sample, which may be excited at lower current densities before the final arc conditions are established.

In the arc, excitation occurs mainly as a result of the thermal energy involved (Mannkopff, 1932), and numerous workers have attempted to estimate the temperatures reached. Values of the order of 7000°K for the temperature of the inner arc column between carbon electrodes were found experimentally by Duffendack and La Rue (1941) and theoretically by Mannkopff (1943). According to Duffendack and La Rue the temperature is independent of current and gap length.

The number of lines excited in the arc is such that unless adequate dispersion is provided by the spectrograph, coincidences may occur between lines of different constituents. Thus whilst in the flame only some 10 to 20 Fe lines are observed, those excited in the arc run into thousands, and over the wavelength range 2000-10,000A Harrison (1939 a) records in all some 100,000 lines, most of which are visible in an arc source. For most biological materials and particularly for soils, rocks and samples with an appreciable iron content, an adequately large spectrograph is required before satisfactory determinations can be made. Of the instruments currently available in Britain only the Littrow type Hilger Large Quartz Spectrograph is to be recommended for intensive arc work, although certain elements may be determined using a Medium instrument.

In the d.c. arc between similar electrodes the conditions at the anode and cathode are quite distinct. Thus with carbon electrodes the anode is seen to be much hotter than the cathode and burns away much more quickly. Whilst the whole of the anode appears white hot, there is on the cathode only one hot point to which the arc strikes and which may travel irregularly over the cathode surface if the shape permits. To this movement of the cathode spot is ascribed the difficulty of making accurate determinations of metals and alloys in the arc (Walsh, 1946). With filled carbon electrodes, however, the wandering of the arc spot can be avoided to a large extent by making the cathode very narrow. The fact that the anode is hotter and burns away more quickly led many workers to place the sample in the anode in order

to increase sensitivity, but, as Mannkopff and Peters (1931) have shown, the greatest emission occurs with most elements in the neighbourhood of the cathode, so that, except in certain instances such as the detection of F by CaF bands, nothing appears to be gained by using the anode as carrier electrode, and sensitivity may in fact be lost. There is the added disadvantage of increased continuous background radiation from the brightly incandescent anode.

As the essential process in arc and spark methods is the production of an electrical discharge over the gap between a pair of conductors, and as biological or soil materials are essentially non-conducting powders or liquids, some form of carrier electrode has to be provided, precautions being taken to ensure that the spectrum produced is a true representation of the sample filled into the carrier electrode. It is this which in general rules out spark methods for such work, as the spark discharge is much more selective and non-reproducible than the arc with such electrodes. At the same time it is often essential for the detection and determination of trace constituents to work at the greatest possible sensitivity : the sensitivity for most elements is considerably greater in the arc than in the spark.

The choice of the technique to be adopted for any particular determination is governed by the element or elements to be determined, and will be the compromise which appears to be best suited to the object of the investigation. Equally good results might well be got from a quite different set of conditions, and it is seldom that two independent investigators will report precisely the same conditions as being best for a particular problem. The possible variables include the electrode material, the polarity of the filled electrode, the arc current, the length of the arc gap, the dimensions of the electrodes, whether the discharge is continuous or intermittent, the duration of the discharge, the section of the arc column from which light is admitted into the spectrograph and whether any diluent or spectroscopic buffer is employed. Thus while it is hoped to indicate some of the different variations which have been suggested only the more important can receive more than brief mention.

b. Production and Control of the Arc Source

Arc sources in use at the Macaulay Institute have been operated from direct current derived from a rotary convertor supplying up to 20 amp. at 250 volts from 400 volt three phase alternating current mains and also from a Westinghouse Westalite Rectifier Type R3TF.224/14 supplying up to 14 amp. at 250 volts, also operated from 400 volt three phase a.c. mains. Both sources have proved very satisfactory. The rectifier is more convenient in operation, being quiet and without moving parts. Results obtained from the two sources of supply do not differ within the limits of accuracy of the spectrographic methods. It is desirable to have a source capable of supplying at least 10 amp., and this cannot be obtained from many of the units commercially available for spectrographic work, but which were designed for d.c. arc work on metals and alloys where lower currents were considered

adequate. The possibility of designing a rectifier unit to provide constant current to an arc without the use of a ballast resistance may be mentioned at this point. Examples of this type are the Raytheon rectifier with a current limiting transformer giving 5 amp. at 60 volts (Brode, 1943) and the Hilger constant current arc source F1330, also giving a 5 amp. supply. Hampton and Campbell (1944) have described an arc circuit controlled by an automatic, solenoid operated, carbon pile resistance in series with the arc, and adjusted to operate at 15 amps. This device is automatic to within $\pm 2\%$.

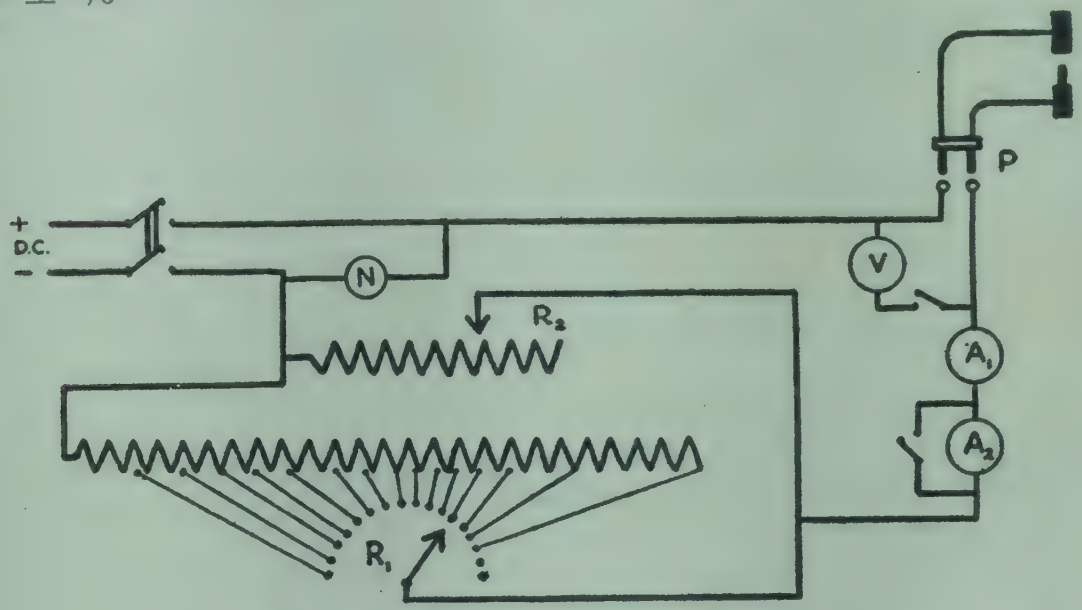

FIG. 18.—Circuit for the control of a d.c. arc

A_1	:	Ammeter 0-15 amp.
A_2	:	Ammeter 0-4 amp.
V	:	Voltmeter 0-120 volt
N	:	Neon indicator
R_1	:	Tapped resistance
R_2	:	Variable resistance
P	:	Polarity reversal plug

The circuit employed at the Macaulay Institute is illustrated in Fig. 18. Over the output side of the main double pole 30 amp. switch is connected a neon indicator which is mounted on a board beside the meters and clock. One lead goes directly from the switch to one side of a 15 amp. 2 pin socket which allows the polarity of the electrodes to be changed merely by reversing the plug. The other output lead passes to the main ballast resistance which is a 15-110 ohm tapped resistance capable of carrying 15 amp. and made by the Cressall Manufacturing Co., Ltd., of Birmingham. This resistance has tappings at approximately 15, 16, 17, 18, 19, 21, 23, 25, 28, 34, 40, 52, 64, 84 and 110 ohms, and is fitted with three blank studs at the high resistance end to reduce arcing when the current is being cut off. In parallel with the tapped resistance is a Zenith Sliding Resistance (190 ohms, 2.8 amp.), fitted with a lead screw and a stop to prevent currents of over 2.8 amp. being passed. This resistance allows smooth and exact adjustment of the current within the steps of the tapped resistance. From the resistance the

FIG. 19.—Control panel for the d.c. arc, with ammeters, voltmeter, neon indicator and clock. The arc positioning screen is on the right. Main switch and resistances are situated to the left of the operator

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supply passes through 2 moving coil ammeters, one of 0-15 amp. (G.E.C. M8103) and one of 0-4 amp. (G.E.C. M8099A), the latter being shunted by means of a shorting plug when the usual higher currents are being used, but it is useful for the accurate measurement of currents up to 4 amp. A voltmeter (Weston 280 or G.E.C. M8082) measuring 0-120 volts and fitted with a push button switch so that it does not receive the higher voltages over the arc gap before the arc is struck, connected over the polarity reversal socket, completes the circuit. The arrangement of the instrument panel is seen in Fig. 19. The clock is by Smith's English Clocks Ltd., being Process Timer PTM/2, which runs for up to 20 minutes and is operated by cords taken to the front of the table. The switch beside these operates the one-minute sector mentioned below (see p. 79). Process Timer ST is the only similar clock currently available.

The arc stand illustrated (Fig. 20a) was designed in Göttingen for use in the cathode layer arc method and can be obtained from Messrs. Fraser & McKay, Upperkirkgate, Aberdeen. It provides all necessary adjustments in close proximity and allows of quick and easy adjustment of the arc position. It is suitable only for low voltage arc work. One essential requirement of a stand for arc work is the provision of a detachable key to the electrode fixing screws, or some other means of heat insulation. Many commercially available designs ignore this point completely. The Hilger Gramont Stand can be modified by the use of adaptors such as are described by Strock (1936 a). A modified Hilger stand is illustrated in Fig. 20b. Most types of arc stand designed for general use follow Gramont's original model (Breckpot, 1936 b, Clayton, 1941). Various workers have suggested methods which bring series of samples into position one by one (Quill and Selwood, 1929, Spencer, 1931, Owsley and McReynolds, 1942), whilst stands of various types are described by Gatterer (1939), Pierce, Torres and Marshall (1940) and Scribner and Corliss (1943). Provision for rotating the lower electrode is made by Jaycox and Ruehle (1940 a, b) and Owsley and McReynolds (1942), whilst water cooled jaws are described by Lindemann (1935), Owens (1938 b), Sawyer and Vincent (1940) and Scribner and Corliss (1943). A stand which is designed particularly for high voltage a.c. arc work is described by Duffendack and Wolfe (1938 a, b) whilst the Petrey stand (Churchill and Churchill, 1941, Churchill, 1944) carries samples such as metal plates or briquetted pellet samples (Churchill and Russell, 1945) as the upper electrode. The arc stand should have fitted above it an efficient hood to remove fumes such as carbon monoxide and nitrous gases and, more important, the material burnt in the arc, that would otherwise contaminate the laboratory. A 6″ Vent-axia fan fitted with a 3″ suction pipe leading to a hood, about 12″ across, and 6″ above the level of the arc has proved efficient. In addition to removing fumes, the slight draught stabilizes the arc considerably and minimizes the effect of movement in the laboratory during an exposure.

A completely enclosed arc stand is unnecessary for low voltage d.c. arc work, and makes operation inconvenient. The operator should however

be screened from the direct ultra-violet emission by means of a suitably placed coloured glass screen.

An optical bench to carry the arc stand and lenses is essential to ensure accurate positioning of the arc. The working position of the arc is best controlled optically by means of a lens which projects an enlarged image of the arc onto a marked screen. An off-set glass lens, available with the Hilger Large Quartz Spectrograph, gives an image on a screen beside the slit, but it has been found more convenient to have this control on a screen beyond the arc and adjacent to the control panel carrying the ammeters and clock. A 20 cm. focal length convex glass lens gives a suitable image when mounted 27 cm. from the arc, with the screen 65 cm. from the lens. The image of the arc on the screen is kept in position during an exposure by the use of light from the arc itself ; if it is necessary to position the arc accurately before commencing an exposure an electric bulb can be used to project a shadow image of the electrodes onto the screen.

The proper positioning of the arc depends on the investigation being carried out. The line image on the plate is a reproduction of the conditions prevailing at the slit of the spectrograph, and there are two extreme possibilities. Either the slit can be illuminated evenly from end to end by light from all desired parts of the arc column, this being the necessary condition for photometric measurement, or at the slit the light distribution can correspond to that in the arc column, so that the spectrogram records this distribution. For the latter condition, which is generally preferred for qualitative and often for semi-quantitative work, an image of the arc is produced at the slit by means of a short focus spherical or sphero-cylindrical lens. By observation of the position of the image relative to the slit, the arc position can be adjusted to allow the desired portion of the arc column to be recorded on the plate. When this position is found, the necessary markings are made on the screen so that this position can be accurately reproduced. The sphero-cylindrical lens is computed to give the actual light distribution in one direction whilst in the other the emission is spread diffusely. When this diffuse band is arranged horizontally it helps to minimize effects due to wandering of the arc.

The simplest means of obtaining an evenly illuminated slit, such as is required for step sector or logarithmic sector work, found to be satisfactory at the Macaulay Institute with an E.1 spectrograph, is to produce an image of the arc at the collimator of the spectrograph by means of a long focus lens just in front of the slit. A mask can be fitted at the collimator to select the portion of the arc column that it is desired to use. More elaborate methods of achieving even slit illumination involving the use of two or three lenses, or a lens-mirror combination, together with external masking screens have been described. In the method illustrated by Strock (1936 a) a spherical (or sphero-cylindrical) lens, such as is normally used to image the arc on the slit, produces an image of the arc on a screen with a variable aperture, which is placed in the position normally occupied by the light

FIG. 20.— (a) Arc stand designed for use with the d.c. arc

(b) A modified Hilger arc stand

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source. A long focus lens just in front of the slit produces an image of the aperture at the collimator. An aluminized concave mirror behind the source to take the place of the first lens in the above set-up is also supplied by Hilger. With a mirror, achromatism is attained without the use of quartz-fluorspar or quartz-rocksalt lenses, which would be very expensive (Twyman, 1941).

Zeiss (1938) have described a lens system to produce even slit illumination which requires 3 lenses between source and slit. This arrangement was used by Rankama and Joensuu (1946).

Twyman and Simeon (1930) described a system with two lenses together at the slit, the sector being placed in the zone of parallel light between them. They drew attention to the point that any attempt to attain even density of the slit image must fail if the slit jaws are not perfectly parallel and clean.

c. Electrodes

For the analysis of non-conducting powders, and to a great extent also of solutions evaporated on the electrodes, the only electrode material suitable for general use is some form of carbon. The chief element with which contamination difficulties are experienced when using carbon or graphite electrodes is boron, which in the form of boron carbide would appear to be exceedingly difficult to eliminate once it is present. For the analysis of boron, copper electrodes are generally employed, although expensive B-free carbon and graphite can be obtained.

There would appear from the literature to be considerable confusion between graphite and carbon electrodes and it is often difficult to ascertain which modification of carbon is actually employed—thus Hasler (1941) in the description of the high streaming velocity electrode refers to carbon in the text and graphite in the diagrams of the electrode. It is necessary that the distinction should be made clear, owing to the differing behaviour of carbon and graphite electrodes when burnt under similar conditions. The difference in behaviour is probably due, as suggested by Preuss (1935), to the difference in thermal conductivity of the two forms of carbon, and it is unfortunate that the name of the element itself should have to be applied to one of the modifications in common use for spectrographic work. There is considerable difference in the rate of burning of similarly shaped carbon or graphite electrodes, the latter being consumed much more slowly, with considerably more wandering of the arc. Carbon is therefore more suitable than graphite for the analysis of materials which are packed into a boring in the electrode and which are introduced into the arc column as the electrode material is burnt away. One disadvantage of carbon is that it is rather more difficult to shape than graphite. Both forms are obtainable in a degree of purity adequate for most quantitative spectrographic purposes.

The testing of the purity of an electrode material is not simply a matter of burning empty electrodes under the same conditions of current,

electrode dimensions and time of exposure as are to be employed for the proposed determination. Some elements present in trace amounts are more easily excited when other ions are present in the electrode or arc column, whilst others appear to be most sensitive on carbon alone. Thus Webb (1937 b) and Webb and Fearon (1937) point out that the "latent impurities" Ti, V and Li in graphite are enhanced in the presence of the alkali metals, although they may scarcely be visible in the electrodes themselves. The effect is also recorded by Maltby (1937), Borovick and Borovick-Romanova (1937 a) and Bertrand (1942) and may, according to Daniel and Hewston (1942), be responsible for many erroneous reports of vanadium in biological materials.

The method of purification of electrodes by burning off impurities before addition of the sample is possibly less efficient than has been claimed, as the diminution of intensity of some trace element lines may be due to the evaporation of other elements. The burning-off process has been used by Standen and Kovach (1935) and by Zurrer and Treadwell (1935), the latter employing a 12 amp. arc in an atmosphere of argon or nitrogen. Smith (1946) questions whether it is surface or internal impurities which are removed. It may have a definite value, as claimed by Jaycox (1945), in making the electrode porous prior to the addition of solution samples, but, on the other hand, numerous other workers intentionally render the electrode non-porous by addition of wax or kerosene.

Electrodes of spectrographic purity are available from numerous sources, but for many purposes it is more economical, where facilities are available, to purify less expensive types of carbon or graphite. For certain qualitative or quantitative purposes Prokofiev (1943) has suggested that very cheap electrodes can be made by heating lime or birch wood sticks for two hours at over 800°C.

There are two means by which carbon can be purified, heat treatment and solvent extraction. Heat treatment in some form or other would appear to be both simpler and more efficient. Heyne (1930, 1932) has described methods for indirect heating in a carbon tube furnace in an atmosphere of inert gas or carbon tetrachloride, and also for direct electric heating of the rods by passing an electric current through them. The latter method has been developed by Preuss (1935) and also by Bauer and Hörmann (unpublished) in Göttingen, and electrodes so prepared were commercially available from Ruhstrat of Göttingen. Preuss used a current of 180 amp. through a 350 mm. long 5 mm. diameter carbon rod. The current falls slowly as the outer layer of carbon is converted to graphite. Preuss used times of over 30 seconds at the current of 180 amp. Rusanov (1934 a), using a similar method but reporting rod temperature rather than current, found that most impurities were lost at 2700°C. in 10-20 seconds. Rusanov and Kostrikin (1940) with a 110 volt supply used from 100 to 420 amp. for 30 to 40 seconds. Gatterer (1941), in a review of possible methods, has also preferred heating by passing the current directly through

the rods to be purified and has recommended, for 5 mm. diameter rods, a current density of 15 amp. per square mm. This is equivalent to a 70 volt, 300 amp. current through a 150 mm. rod. Rods are conveniently held in graphite blocks during purification.

This method of purification has been studied by Hoogland (1946), Schmidt (1946) and Deinum (1946) in three complementary papers. Hoogland obtained adequate purity by heating for 60 seconds with a maximum current of 650 amp. and a current density of 17 amp. per sq. mm. Schmidt found that such rods were not suitable for impregnation with solution, following the Scheibe and Rivas (1936) technique, and recommends heating with a 48 volt a.c. supply, with a 26 kw. input which diminishes to 17 kw. after two minutes. Deinum points out the liability of rods to explode violently at high currents (above 660 amp.).

Carbon so purified generally contains B, and only slightest traces of other impurities such as Ti and Si, and then only if the starting material contained appreciable quantities of these elements. Carbon rods suitable for most spectrographic purposes and purified by this method are obtainable from Messrs. C. H. Champion and Co., Ltd.

Purification by indirect heating in an evacuated furnace is used by Owens (1938 a, b) and the Dow Chemical Company (1938), treatment in an evacuated furnace for several minutes at about 2500°C. at pressures of 2-10 inches of mercury removing Ca, Cu, Al, Ti and V and nearly all the Fe and Si.

Numerous authors have attempted the chemical extraction of impurities from carbon or graphite by steeping in or refluxing with suitable reagents. Standen and Kovach (1935) boiled rods in aqua regia, treated with concentrated ammonia, then heated in ammonia and chlorine at 1000-1100°C. Staud and Ruehle (1938) heated cut electrodes in a silica dish, cooled and refluxed with 1 : 1 sulphuric acid for 24 hours, then washed 2-4 times with boiling distilled water. This was reported to remove Al, Ca, Cu, Fe, Mg, Mn, Ag, Ti and V from graphite, but to leave B and Si. Cholak and Story (1938) steeped rods in a 1 : 1 mixture of hydrochloric and nitric acids at 70°C. for 48 hours, changing the solution 4-5 times, then in 4 or 5 changes of distilled water at 70°C. and finally heated in a muffle at 1000°C. for one hour. B, Si, Mg and V were left in the electrodes. Bell (1938) refluxed graphite with nitric acid alone.

For all except purely qualitative examination, the dimensions of the electrode carrying the sample should be the same for unknowns and standards and, in order to achieve this, some form of electrode cutter is essential unless the work of making the electrodes is to be tedious and costly. The shape of the electrode is chosen with the aim of the investigation and the nature of the material to be examined in mind. Thus for liquids to be analysed in the high voltage a.c. arc, flat ended rods are adequate, as one drop dried on each electrode is generally sufficient. The possibilities of variation in shape where larger volumes of liquid, or a solid

powder, are filled into a boring in the electrode, are innumerable. The simplest type of boring is a shallow depression with the outer diameter of the rod untouched, but this assumes that the original rods are of uniform size and also that accurate centering of the depression can be obtained. If the boring is off centre the burn will invariably be poor, as the electrode will burn away at the thin walled portion. Numerous tools have been described for simultaneously boring to the required depth and cutting the walls to the required thickness. Myers and Brunstetter (1939) formed electrodes of 6 mm. inside diameter, 3.5 mm. deep with 0.3 mm. wall, from 8 mm. rod. Shallow thin walled craters in graphite are given by a shaping lathe described by Majors and Hopper (1941). Oshry, Ballard and Schrenk (1942) give details of a cutter for 3.2 mm. diameter electrodes with a crater 1.3 mm. diameter and 1.5 mm. deep from 4.75 mm. rods. The cutter described by Hampton and Campbell (1944) is mounted directly to a motor, which for convenience should be fitted with an automatic break (Saunderson and Caldecourt, 1944). Hodge (1942) made no provision for cutting the outside wall. Amongst cutters for unusually shaped electrodes is that of Eastmond (1944) for one with a high centre pillar. Some of the graphite electrode shapes which have been used for specialized purposes are illustrated by Churchill (1945). The possibility of cutting a narrow neck below the crater to increase electrode temperature is shown. As graphite is easier to work than carbon, the most complicated shapes have generally been fashioned in this material.

For the cathode layer arc method, using carbon electrodes with a deep narrow boring, a cutter designed in Goldschmidt's laboratory in Oslo has been used at the Macaulay Institute. The details of the electrode used for ordinary purposes are: 5 mm. carbon rod 25 mm. long is cut down over its upper 15 mm. to 2.8 mm. diameter with a crater 8 mm. deep and 0.8 mm. diameter. The lathe tool carries a 0.8 mm. ($\frac{1}{32}$ inch) drill and three radial cutting tools which are adjustable to allow for wear. This is quite severe and sharpened tools may require replacement after cutting 100-200 electrodes. This cutter is illustrated in Fig. 21.

Electrodes with wide shallow borings are easily filled by pressing the electrode into the sample or simply by pouring the sample into the crater and compressing it with a suitable tool. For deep narrow craters a convenient method is that given on page 80. Feldman (1944) has described an easily cleaned measure for powders.

Lewis (1932) employed a compressed pellet of the sample in the electrode. Dietert (1941) and Churchill and Russell (1945) have used pellets to replace electrodes in spark analysis of ores, powders and powdered metals, binders and conducting material being incorporated. A simple pellet press is described by Harrison and Ralph (1943).

Where solutions are pipetted into the electrode cavity and evaporated, the electrode is frequently first treated with a material to make it non-absorbent. Amongst the materials suggested are paraffin or heavy mineral

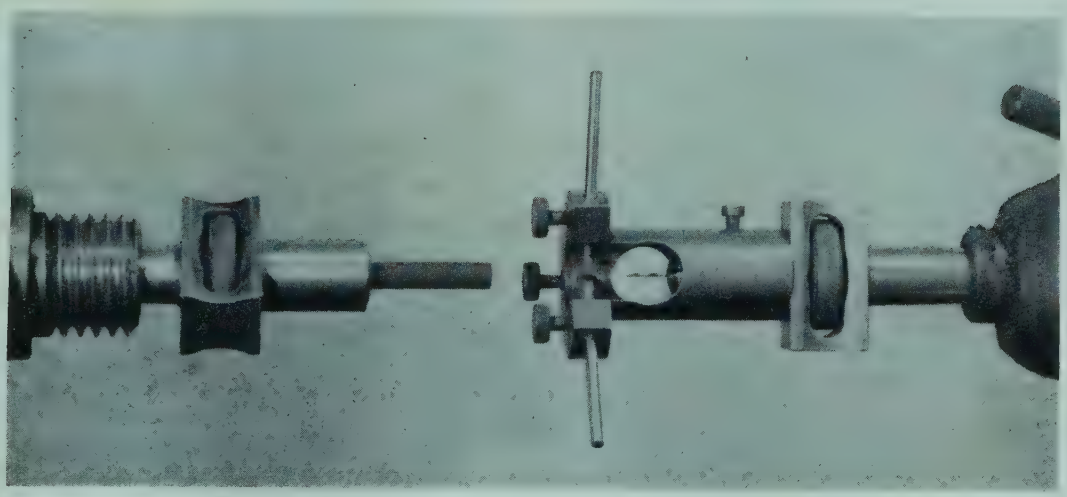

FIG. 21.—Electrode cutter for preparing electrodes for the cathode layer technique, mounted on a $3\frac{1}{2}$in. lathe

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oil (Wilhelm, 1938), wax (Mackenzie, 1939), kerosene (Brunstetter, Myers, Wilkins and Hein, 1939) and acryloid lacquer (Hampton and Campbell, 1944). Oertel (1944 b) has described an electrically heated metal block for evaporating solutions added to electrodes.

d. Qualitative Analysis

Qualitative analysis involves the examination of the completed spectrogram in order to ascertain which constituents are present. This can be considered independently of the mode of production of the spectrogram. Normally, however, the source would be some form of arc, the cathode layer direct current arc (see Chapter 6) being particularly suited for such work.

The qualitative interpretation of any spectrogram may involve anything from the identification of the metallic radical in some simple substance to the detection of some 30 to 40 constituents present in very different amounts in a complex mixture. The former problem is generally only a question of a rapid visual inspection of the spectrogram, as an analyst will soon become familiar with the characteristic line groupings of the commoner elements such as are illustrated in the small atlas of Löwe (1936). For more detailed spectrograms the large atlases of Gatterer and Junkes (1945, 1947) are excellent and when their third volume is completed practically all the elements will have been covered.

For the detection of all the elements which are present in a complex material in amounts above the spectrographic sensitivity the problem is much more involved. It is clearly impossible to identify all the lines present in each spectrogram which is examined : an arc spectrogram of a material such as iron may show several thousand lines of that element. There are, however, certain lines of each element which are more sensitive than others in that they remain visible to lower concentrations of the element. The persistent lines (Hartley, 1884), *raies sensibles* or *raies ultimes* (Gramont, 1920), *letzte Linien* (Gerlach, 1925), sensitive lines or principal lines as they have been variously called, have been listed by numerous workers, and several sets of these tables have been collected by Twyman and Smith (1931).

Amongst earlier workers there was some discussion as to whether the most persistent lines were actually strongest at all concentrations, as such factors as self reversal of the strong lines were complicating their observations. The best discussion of principal lines is to be found in papers by Meggers (1941 a, b).

In the consideration of spectral intensity and relative line intensities, it must be borne in mind that the recorded image depends both on the intensity of the line and the sensitivity of the photographic emulsion at the wavelength in question.

The procedure in the examination of any complex mixture is to search for one or more of the persistent lines of each element. In certain instances one line alone may be sufficient to give unequivocal proof of the presence

of the element concerned, but in others the possibility of coincidence of wavelength between the line in question and that of another element may make the identification uncertain. Further lines must then be examined, and attention paid to the relative densities of the lines concerned, before the identification can be considered proved. This type of inspection is difficult by purely visual means and the assistance of a spectrum comparator or projector is generally desirable. Reference to an adequate table of wavelengths such as that of Harrison (1939 a) is necessary to determine whether a coincidence is possible or not. For some purposes the shorter tables of Kayser and Ritschl (1939) may be adequate.

Apart from the tables of persistent lines in Twyman and Smith (1931), there are one or two other compilations which are of interest including those of Moritz (1933), Gerlach and Riedl (1936), Tongeren (1938), Williams (1939), Azcona (1941 b) and Standen (1944).

The interpretation of a single spectrogram may be facilitated, before one is in a position to recognize the line dispositions at a glance, by the inclusion on the plate of a wavelength scale which can be produced from the built-in scale fitted to certain smaller types of spectrograph, but, for materials such as soils and plant ashes, the worker will generally rely, for primary orientation as regards wavelength and location of the lines of the trace constituents, on the characteristic groupings of the lines of the major constituents. Certain groups of lines are quite unmistakable and are soon committed to memory as the first step in the development of spectrographic methods. Groups which might be memorized for quick orientation in the 2480-8000A wavelength range are :—

Boron	2 lines	2496.8, 2497.7
Silicon	6 lines	2506.9, 2514.3, 2516.1, 2519.2, 2524.1, 2528.5
Aluminium	2 lines	2568.0, 2575.1
Aluminium	2 lines	2652.5, 2660.4
Magnesium	5 lines	2776.7, 2778.3, 2779.8, 2781.4, 2783.0
Magnesium	2 lines	2795.5, 2802.7
Magnesium	1 line	2852.1
Silicon	1 line	2881.6
Iron	6 lines	3016.2, 3017.6, 3019.0, 3020.5, 3020.7, 3021.1
Aluminium	2 lines	3082.2, 3092.7
Iron	3 lines	3099.9, 3100.3, 3100.7
Calcium	2 lines	3158.9, 3179.3
Copper	2 lines	3247.5, 3274.0
Sodium	2 lines	3302.3, 3303.0
Iron	2 lines	3306.0, 3306.4
Iron	2 lines	3440.6, 3441.0
CN	band head	3590.4
CN	band head	3883.4

Calcium	2 lines	3933.7, 3968.5
Aluminium	2 lines	3944.0, 3961.5
Manganese	3 lines	4030.8, 4033.1, 4034.5
Potassium	2 lines	4044.2, 4047.2
CN	band head	4216.0
Calcium	1 line	4226.7
Calcium	5 lines	4425.4, 4435.0, 4435.7, 4454.8, 4455.9
Calcium	3 lines	4578.6, 4581.4, 4585.9
Titanium	4 lines	4981.7, 4991.1, 4999.5, 5007.2
Calcium	3 lines	5264.2, 5265.6, 5270.3
Sodium	2 lines	5890.0, 5895.9
Lithium	1 line	6707.8
Potassium	2 lines	7664.9, 7699.0
Sodium	2 lines	8183.3, 8194.8

All these groups should be easily identified in the d.c. arc spectrogram of any soil in a carbon electrode and are marked in Appendix III. The initial location of the groups can be made either from a wavelength scale or from a comparison Fe spectrum, carried in juxtaposition to the soil spectrum on the same plate by means of exposures through adjoining sections of a Hartmann diaphragm. This device, which forms part of the slit of Hilger spectrographs, enables three spectrograms to be recorded side by side, with a slight overlap, in absolute register. This is often not quite obtained if the movement is made by racking the plate holder. A means of recording the Fe spectrogram simultaneously with the unknown, by the use of a quartz prism at the slit, has been described (Mitchell, 1940) and employed to produce the spectrograms of Appendix III. The wavelengths of the Fe lines are obtained from calibrated Fe spectrograms such as are supplied by Hilger or are to be found in Brode (1943) or Gatterer and Junkes (1935).

The list given above is not intended to indicate the strongest lines of the elements mentioned, but is merely a guide from which the position of the analysis lines of trace constituents can be found. Many individual trace constituent lines, such as Co 3453.5A, Ni 3414.8A, Mo 3170.3A, Cr 4254.3A, Pb 2833.1A, Sn 2840.0A, can be memorized and identified in a like manner from the configuration of the adjoining lines of the major constituents.

In the inspection of an unknown spectrogram, the general practice is to compare it with a marked plate or a spectrum chart carrying a spectrogram of a similar type of material, that is, with the same major constituents and a convenient amount of as many trace constituents as possible. Chang (1939) describes the preparation of a standard plate of this type. A very convenient material for soil work is town refuse dust, the finest screenings from the refuse separators in which most of the trace constituents likely to be found in soils occur in a suitable silicate matrix, and to which those absent can easily be added. In Appendix III is reproduced a spectrogram of such a material in which the location of the more important trace con-

stituent lines is indicated. R.U. powder is marketed by Johnson-Matthey for the same purpose, but the base of ZnO, MgO and CaO is not convenient for comparison with the silicate base of soils or the alkali and alkaline earth phosphate base of plant ash. The photographic enlargement of the R.U. arc spectrum and the list of the sensitive arc lines of 50 elements contained in R.U. powder (Ryde and Jenkins, 1929) are both useful. The former carries a comparison Fe spectrum.

A rather similar powder with a silica base is proposed by Tongeren (1938) who was, however, limited to the visible portion of the spectrum by the use of a glass spectrograph, so that the quantities which he suggests would prove excessive for certain elements such as Ag and Sn, when the more sensitive ultra-violet lines are used.

Direct comparison of two spectrograms on different plates is not easy, whilst it is not practicable to carry a comparison standard adjoining each unknown spectrogram, so that some form of spectrum comparator should be available. The type most commonly employed in Britain is the Hilger Judd Lewis Spectrum Comparator (Lewis, 1936). A simpler form was described by Jack (1930) and it has recently been modified by Mather (1945). The first description of this type of comparator would appear to be that of Hartmann (1906) who used it in astronomical work for measuring line shift. In this type of instrument, images of portions of two plates are brought together in one eyepiece by means of a series of reflecting prisms or mirrors and two objectives. By bringing the lines of the major constituents of the two spectrograms into correspondence in the two halves of the eyepiece the presence or absence in the spectrogram being examined of the lines of a constituent present and marked in the standard comparison plate can be established. A similar device using a bi-prism or a refracting unit is described by Davis (1939).

For purposes of demonstration this comparator is not so convenient as a projection-comparator which provides images of two spectrograms side by side on a screen. A suitable design is that of Gatterer (1938, 1940), whilst Vincent and Sawyer (1941) and Dietert and Schuch (1941) have both incorporated a projection-comparator into their microphotometers, the latter being the A.R.L.-Dietert instrument. Edlin (1934) has pointed out that it is possible to obtain the same effect by projecting two spectrograms placed face to face.

It is often simpler and more convenient to have the comparison spectrum as a photographic enlargement, or as a diagram on the same scale as the projected image and to use this as part of the screen. Numerous workers have described this method, including Lasegue and Collin (1930), Scheibe (1933), Pierce, Torres and Marshall (1939), Nickolls (1943) and Brode (1943), the latter reproducing a spectrum chart of this type with an Fe comparison spectrum and the positions of the lines of other elements indicated diagrammatically, with a blank space for the projected image between them.

In the spectrograms obtained with a large quartz spectrograph from soils, plant materials, rocks and fertilizers there is seldom any dubiety regarding the identification of the lines of the trace elements normally present when such comparators are employed. It is when high contents of line-rich elements such as Mn, Co, Ni or the rare earths are encountered in unusual materials that dubiety may arise.

Table 3 (see p. 84) lists the lines used for the identification of the trace constituents sought in soil work, when excitation is by the cathode layer direct current arc. The lines given are in many instances those which have been found to be suitable for both qualitative and quantitative work.

The use of a spectrum comparator avoids the tedious method of determining the wavelength of an unknown line by means of a photo-measuring micrometer. Hoxton and Mann (1937) have designed an instrument of this type reading directly in wavelengths or wave numbers, but the simpler models supplied by Hilger are adequate for this work, should it be necessary.

In qualitative analysis valuable information on line identity can often be obtained by consideration of the behaviour of the line itself, either over the length of the arc column or at different times during the exposure. Thus, if the arc source be imaged on the slit, the distribution of intensity of the emission in different sections of the arc column is recorded. Certain elements of high ionization potential, such as B or Be, show lines relatively constant in density over the whole length of the column whilst others such as the alkalis are enhanced in the neighbourhood of the cathode. This cathode layer effect, which is discussed more fully below, often provides a clue to the nature of the line concerned. The time factor, which involves taking more than one exposure during the combustion of the material, distinguishes between volatile and less volatile constituents, lines of such elements as Zn, Sn and Pb showing maximum intensity in the initial stages of the burn whilst others, such as Zr or the rare earths, are most intense towards the end. Strock and Heggen (1947) have illustrated the part which this fractional distillation can play if samples are not burned to completion in the arc.

Whilst a qualitative inspection of a sample is seldom adequate for the type of differentiation required in soil and plant analysis, any subsequent semi-quantitative or quantitative determination depends on accurate identification of the lines of the elements involved, and on those chosen not being interfered with as a result of coincidence with lines of other elements, so that before proceeding to such analyses a good acquaintance with the methods of qualitative analysis is required. It is sometimes claimed (Churchill, 1945; Chirnside, 1945) that qualitative examination is the most important application of spectrographic analysis, but it is only in isolated instances such as the initial detection of Mo in the "teart" pastures of Somerset, by Ferguson, Lewis and Watson (1943) that some form of quantitative analysis is not required. It is in fact difficult after some

experience with spectrographic methods to avoid making some assessment of the amount present when doing qualitative work, and with very little extra labour it is possible to make semi-quantitative estimations of most constituents present in materials of known composition for which suitable comparison standards are available.

e. Semi-quantitative Analysis

By semi-quantitative determination is generally meant an estimation of the content of any element, by visual means and liable to subjective errors, by comparison with standard spectrograms of similar material, without the aid of photoelectric measuring equipment. There are several ways in which this can be carried out. The simplest is by direct visual comparison of the spectrogram of the unknown with those of standards, and this method is discussed fully below in dealing with the semi-quantitative determination of the content of trace constituents in soils, rocks and plant ashes. For this a spectrum comparator is essential. The method of assessment is to compare the density of spectral lines in the unknown with those in standards and so to assess the content in the unknown. The standard spectrograms are made, under precisely the same conditions as the unknown, from a series of mixtures with the same major composition as the unknown, and with the trace constituents varying from 1 p.p.m. to 1 per cent in steps preferably of $\sqrt{10}$ times, which gives even concentration intervals and a convenient gradation.

Instead of visual comparison of line intensity with standards, the intensity may be estimated visually by means of a step sector (Breckpot, 1933; Strock, 1936 a; Eeckhout, 1945 a, b) or a step filter. The slit of the spectrograph receives exposures in steps of 2, or log 2, covering a 20-100 fold exposure range in 6 or 7 steps. This gives a spectrogram similar to that illustrated in Fig. 22. The weaker lines are visible only in the fully exposed steps, and the number of steps in which a line is visible is taken as a measure of its intensity.

Before the introduction of photoelectric methods, quantitative results were obtained by what would now be classed as a semi-quantitative method. This involved measurement of the length of the spectral line produced when a logarithmic sector was rotated in front of the slit (Scheibe and Neuhäusser, 1928; Twyman and Simeon, 1930). This method is still used occasionally (Wander and Brode, 1941; Ahrens, 1942; Rankama and Joensuu, 1946). The chief drawback is the difficulty in deciding the point of disappearance of the tip of the line to which the measurement is made, and it is here that subjective errors arise.

With a line-rich element it is possible to devise a method of semi-quantitative estimation by counting the number of lines of the element that are visible, as has been suggested by Oertel (1937) for cobalt in soils. Bennewitz and Rötger (1937) make positive prints of the comparison spectrograms, and on superimposing the negative of the unknown the lines

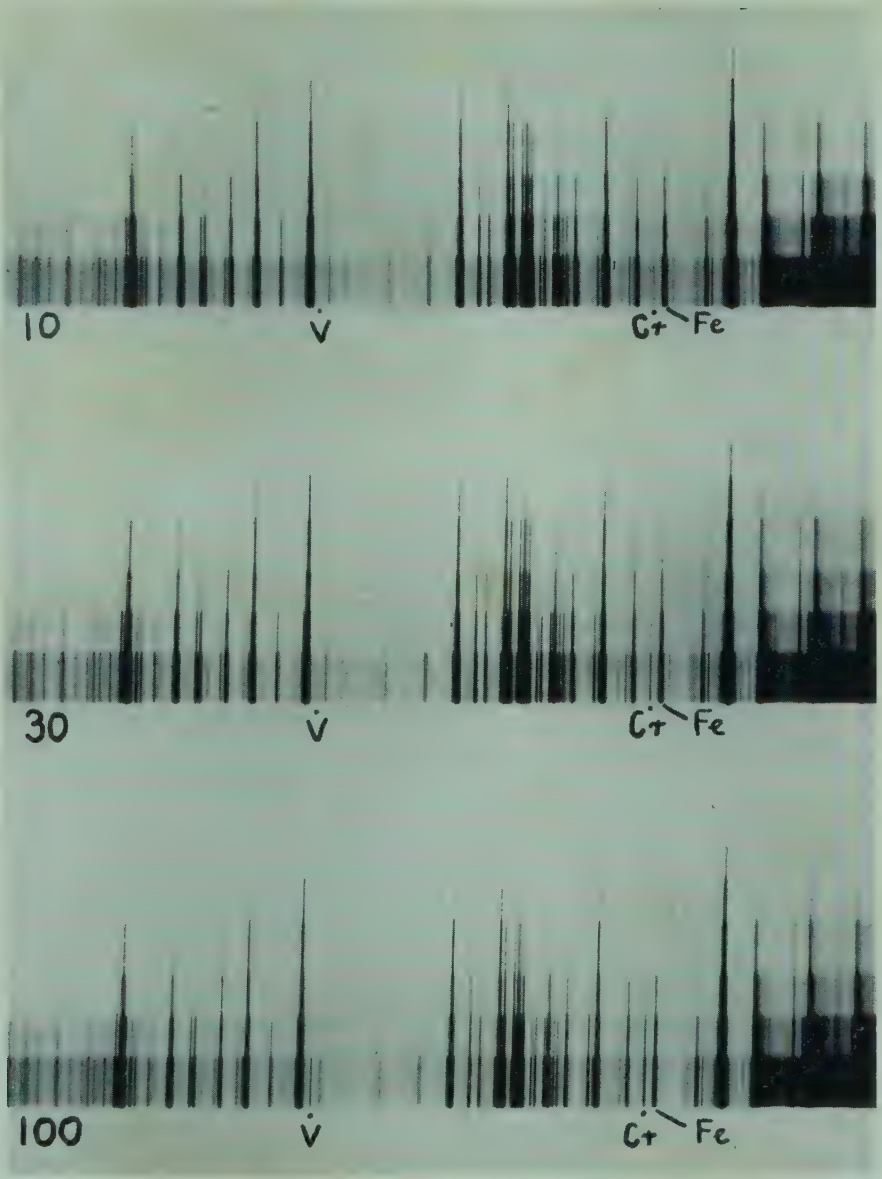

FIG. 22.—Portion of a step spectrogram showing lines of V 4379.24A and Cr 4254.35A at 10, 30 and 100 p.p.m., and the Fe 4250.79A line at 5% Fe_2O_3

[*Facing page 68*

of those trace elements which are present disappear. A semi-quantitative evaluation method is proposed, a series of standards of different trace element content being prepared and from these the one chosen which is masked most exactly by the unknown plate.

Where a trace constituent has to be determined in a base containing a line-rich element, such as iron, in constant amount, the content of the trace constituent can be estimated by finding a line of the major constituent similar in density. This is the method of homologous line pairs proposed by Gerlach and Schweitzer (1930 a), and it can be developed into a truly quantitative method by photoelectric measurement of the densities. This method, alone of the semi-quantitative methods, makes some allowance for variations in source conditions and photographic effects such as change in development or emulsion sensitivity.

All these semi-quantitative methods depend on the use of standard spectrograms prepared under similar conditions from materials as nearly identical in composition as possible with the material being examined. The effect of the variation of the major components of a substance on the intensity of the spectral lines of its trace constituents will be considered in more detail in Chapter 6 and it is sufficient to mention that errors up to tenfold are possible from this cause. Precautions must therefore be taken to ensure that unsuitable comparison standards are not employed. In the ratio-quantitative method, Lewis (1932) describes the gradual synthesis of a material alike in major and trace composition to the unknown.

A preliminary description of a photometric semi-quantitative method has been given by Harvey (1946), a full description being promised in book form. The method requires no prepared standards and provides determinations with a limit of error of 30 to 50% of the amount present. It is based on a d.c. arc method wherein a weighed sample is completely vaporized, selected line-to-background ratios evaluated densitometrically, and the ratios multiplied by sensitivity factors for particular spectrum lines in a particular matrix. Sensitivity factors have been evaluated for Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cb, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Ru, Sb, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn and Zr in a variety of matrices which in general consist each of a single one of the above elements. The author of the method claims that with care in setting up spectrographic apparatus and by testing with certain standard samples, these sensitivity factors can either be applied directly or be systematically modified for use in all spectrographic laboratories.

f. The Analysis of Soils, Plant Materials, etc., in the Direct Current Arc

For the qualitative and semi-quantitative examination of soils and plant materials, methods similar to those developed for the examination of rocks and minerals are generally satisfactory. Much work of this type has been done by the cathode layer arc method developed by Goldschmidt

and his collaborators in Oslo and Göttingen, and described in numerous publications such as Preuss (1935), Strock (1936 a) and Tongeren (1938). The method in use at the Macaulay Institute and described in Chapter 6 is a development of this.

Milbourn (1937) used 0.01 g. of finely ground soil or unashed plant material (added in stages if necessary) in the graphite cathode electrode of a very short (1 mm. long) arc run at 7.5 amp. He used a Hilger Medium Quartz Spectrograph and found the following wavelengths suitable for qualitative examination :

Li	6707.9	Hg	2536.5	Nb	3163.4
Na	5890.0	Sc	3613.8	Ta	2656.6
K	7664.9	Y	3242.3	P	2553.4
Rb	7800.3	La	3245.1	As	2349.8
Cs	8521.1	Al	3961.5	Sb	2598.1
Cu	3247.6	Ga	2943.6	Bi	3067.7
Ag	3280.7	In	3256.1	Cr	4254.3
Au	2428.0	Tl	2767.9	Mo	3132.6
Ca	4226.7	Ti	3349.4	W	2656.6
Sr	4607.3	Zr	3438.2	Mn	2798.3
Ba	4554.0	Si	2881.6	Fe	2483.3
Be	2348.6	Ge	2651.1	Co	2424.9
Mg	2852.1	Sn	2840.0	Ni	3414.8
Zn	3345.0	Pb	2833.1	Pt	2659.4
Cd	3261.0	V	3185.4	Te	2385.8

whilst the limits of detection of some elements were, in p.p.m. :

	Li	Rb	Ag	B	Mo	Mn	Co	Ni
In soils	1	500	1	1	10	–	5	1
In plant materials	1	200	–	–	5	1	1	1

For the detection of B, copper electrodes were necessary owing to the presence of B in the graphite, and the line B 2497.7A was employed. Synthetic plant materials were prepared by adding a solution of the element being determined to a mixture of 95% tannic acid and 5% potassium phosphate. A closer approximation to plant material worked out by Ashton is reported by Twyman (1941). Most workers prefer to deal with ashed plant materials and to prepare standards similar in composition to the ash.

An example of the use of the normal d.c. arc technique is the semi-quantitative method described for the analysis of soils, plant ashes, fertilizers and rocks by Ballard (1937; 1938 a, b; 1940 a, b, c ; 1941) and Ballard and Gow (1939). A finely ground sample of from one milligram up to 50 mg. of material is placed in a conical boring (diameter : depth ratio of 2 : 1 for small samples to 1 : 2 for large samples) in a graphite or copper electrode and burnt as the anode, because it is hotter and gives a steadier arc with the electrode shape employed, at from 4-10 amp. For the highest sensitivity a short arc, 2 mm. long, was employed with the arc focused on the slit with a spherical quartz condenser. The effective speed of the large

quartz spectrograph was regulated by the use of rectangular apertures over the condensing lens, allowing the speed to be changed during the course of an exposure. Thus a higher effective speed could be used during the first few seconds whilst the volatile constituents came off. For lower sensitivity but greater reproducibility, a longer arc of 4-5 mm. was focused on the collimator by a condensing lens. Subsequent comparison was against standard plates in a Judd Lewis Comparator, using " elimination plates " of the elements common in agricultural materials (Ca, Mg, Na, K, Al, Mn, Cr, B, Si, P and Fe) to simplify the detection and identification of trace constituents. Ballard found the lines listed by Milbourn and quoted above to be suitable.

The semi-quantitative technique of Rogers and his collaborators in Florida is similar. A small portion of a homogenized soil or plant material (about 10 mg.) is volatilized in the anode of a 220 volt d.c. arc using a current of 9-10 amp. Specially purified graphite electrodes were used and the arc maintained until the sample was completely volatilized. For all lines except Zn 2138A a large quartz or glass spectrograph was used : for Zn a small quartz spectrograph, the arc being imaged on the slit (Gaddum and Rogers, 1936 ; Rogers, Gall, Gaddum and Barnette, 1939 ; Rogers and Hughes, 1940 ; Carrigan and Rogers, 1940).

Semi-quantitative estimation was by direct visual comparison of spectrograms with standards on the same plate. The approximate limits of detection for the various elements were : Ag, Co, Cr, Cu, Ni : 1 p.p.m. ; B, Ba, Be, Mn, Mo, Pb, Sn, Sr, Ti, V, Zn : 10 p.p.m. ; Bi, Cd, La, Sb, Th, Y, Zr : 100 p.p.m. ; As, Cs, Li, W : 1000 p.p.m.

A quantitative method for Zn, with 20 mg. of plant ash, containing added Te as internal standard, burnt in the anode graphite electrode at 9 amp. with a 75% reducing sector, has been described by Rogers (1935), Rogers and Gall (1937) and Rogers, Gall and Barnette (1939). Ratios of the densities of the Zn 2138A and Te 2143A lines are plotted against the logarithm of the Zn content to give a straight line working curve, but no details are given of the derivation of the density from galvanometer deflexion. A similar method for Cu (Rogers, 1939) using Cd 3261A, or preferably Sn 3262A, as internal standard against Cu 3247A or 3274A gave a precision of $\pm$5-6% for the average of five spectrograms.

Guelbenzu, Ruiz and Azcona (1944) burnt 50 mg. of soil in the carbon anode of a d.c. arc run off 220 volt mains, but did not record the current applied or the electrode dimensions. The sample was burnt to completion and the spectrogram from 2400-3700A recorded by a Hilger E.1 Large Quartz spectrograph.

Several methods for the quantitative determination of the major constituents in plant materials have been described. Brunstetter, Myers, Wilkins and Hein (1939) ashed about 10 mg. of dry plant material in a thin-walled graphite electrode at 450°C., treated it with kerosene and hydrochloric acid, and finally dried at 90°C. For standards, solutions were added to

kerosened electrodes. The source was a 14.5 amp. 140 volt d.c. arc with a 1 mm. gap, but the polarity is not indicated. No lens was employed, but intensity was reduced by means of a 7.8% reducing sector. Samples were burnt to completion, this requiring from 60 to 90 seconds. Including standards, 64 spectrograms 1 mm. in width were carried on each plate. Working curves were simply the plot of galvanometer deflexion against logarithm of the concentration. Mg, Mn, Ca, Al, Cu, Na, Fe, K and (from Brunstetter and Myers, 1941) P and B were determined with a precision of the order of $\pm 10\%$. A disadvantage of using a short arc with carbon or graphite electrodes is that, as pointed out by Milbourn (1937), the cyanogen bands are very strong. Ashton (1939), using the Milbourn procedure for the determination of Cr in plant material, with Mo as internal standard, found it necessary to suppress the cyanogen bands by the addition of two parts of PbO for each part of plant material.

Curran, Brunstetter and Myers (1943) have used currents up to 26 amp., whilst Myers and Brunstetter (1947) have proposed a magnetic means of stabilizing the arc. A method rather similar to that of Brunstetter *et al.* has been described by Ewing, Wilson and Hibbard (1937) and Hibbard (1941). The plant material is ashed and treated with HCl, then an aliquot of the solution so obtained, containing added NaCl and NH_4Cl, is introduced into a graphite electrode with a boring 8 mm. in diameter and 7 mm. deep. A 10 amp. arc is employed with the electrode containing the evaporated aliquot positive. Suitable concentrations of standards with 0.1 ml. in the electrode were : P 0.01-10 mg./ml., Fe 0.0005-20 mg./ml., Mn 0.001-5.0 mg./ml., Mg 0.001-5.0 mg./ml., K 1-50 mg./ml., Ca 0.001-5.0 mg./ml. The errors were up to $\pm 10\%$. Standards were carried on each plate and the working curve was of line to background galvanometer deflexion ratio against logarithm of the concentration.

In an earlier determination of Ca in extracts of plant ash, Way and Arthur (1935), developing the method of Nitchie and Standen (1932), added 0.05 ml. of the extract, acidified with HNO_3, to the rough broken surface of a graphite electrode which was made the anode and arced at a commencing current of 6 amp., which fell as the salts evaporated to 4.5 amp. The Ca 5350A line was compared with Sr 5330A (1.75% Sr having been added) and a range of Ca from 0.26-0.52% was covered with an accuracy of $\pm 5\%$. A value for the difference of galvanometer deflexions of line and clear plate was used, the difference of these values for unknown and internal standard being plotted against the logarithm of the calcium concentration.

Webb and Fearon (1937) and Webb (1937 a) used simply a small amount of material spread on the surface of a plain graphite or silver electrode and applied the ratio-quantitative method of assessment (Lewis, 1932) in their analysis of biological materials.

Fox and Goodwin (1941) have used Mo as internal standard for the determination of Si, Al, Fe, K, Ca and Mg in soils and soil solutions. $SrNO_3$ was added to the extent of 97% to the solids, so that the effect of extraneous elements, principally Ca, on the relative intensities of Mo and other elements

should be suppressed. In solutions 3.75% $NaNO_3$ was employed as the spectrographic buffer. A short d.c. arc with the sample in the carbon anode was used.

In a series of investigations on biological materials by methods applicable to solutions derived from most sources, Cholak and his collaborators have generally preferred a d.c. arc with an aliquot of solution dried in a graphite anode. Cholak and Story (1941), using a 10 amp. 60 volt arc from 110 volt d.c. mains with the sample in a boring 10 mm. deep in the positive electrode, report suitable wavelengths and sensitivities of material on the electrode for the 20 elements given in Table 2.

TABLE 2

Persistent Lines and Sensitivities in the Direct Current Arc, from Cholak and Story (1941)

Element	Wavelength	Sensitivity mg. on electrode
Aluminium	3082.16	2×10^{-5}
Antimony	2598.1	4×10^{-4}
Arsenic	2780.2	1×10^{-3}
Bismuth	3067.7	2×10^{-5}
Cadmium	3261.1	4×10^{-4}
Chromium	2986.0	2×10^{-4}
	2835.6	5×10^{-4}
Copper	3274.0	2×10^{-5}
Iron	3020.7	2×10^{-5}
Lead	2833.07	2×10^{-5}
Magnesium	2852.1	1×10^{-5}
	2802.7	2×10^{-5}
Manganese	2801.1	2×10^{-5}
Mercury	2536.5	2×10^{-4}
Nickel	3050.8	4×10^{-4}
Phosphorus	2535.6	5×10^{-3}
Silicon	2881.0	2×10^{-4}
Silver	3280.7	1×10^{-5}
Sodium	3302.0	2×10^{-3}
Thallium	2767.9	2×10^{-5}
Tin	2840.0, 3175.1	2×10^{-5}
Zinc	3302.6, 3345.0	2×10^{-3}

The determination of Pb is described by Cholak (1935 a, b), Cholak, Hubbard, McNary and Story (1937), and Cholak and Story (1938). In the latter paper, the determination of Sn, Al, Cu and Ag is also discussed, the lines and internal standards employed being

Pb	2833.1A	:	Bi	2898.1A
Pb	2873.4	:	Bi	2898.1
Sn	2840.0	:	Bi	2898.1
Al	3082.2	:	Co	3082.6
Cu	3274.0	:	Co	3283.5
Ag	3280.7	:	Co	3283.5

A step sector was employed to extend the analysis range, and opacities instead of densities were measured for the weaker lines, a device also used by Cholak (1937) in the determination of Bi 3067.7A with Zn 3036.0A as internal standard. Cholak and Hubbard (1944 a) discuss the effect of background correction on the determination of Cd and compare spectrographic with polarographic and colorimetric methods. The Mo line at 3209A is employed as internal standard.

Cholak, Hubbard and Story (1943) discuss the determination of Al in biological materials, comparing chemical and spectrographic methods. The Al line at 3082A was employed with Bi 2993A and Bi 3024A as internal standards. A straight line working curve is obtained up to 0.12 mg. Al per 100 ml. of solution added to electrode. The types of materials dealt with in the investigations were foods, bloods, tissues, faeces, waters, plant materials and soils. Kehoe, Cholak and Story (1940 a) quote results for Pb and other elements in materials of all the types mentioned. The material was generally ashed at a temperature below 500°C and the ash treated with HNO_3 or HNO_3 + HCl. An aliquot containing internal standard and spectroscopic buffer was introduced into the electrode cavity. Standards contained the same major constituents.

Determinations along the same general lines in biological ashes have been reported by Bell (1938). The lines Mn 2576.12A ; Fe 3020.65A, 3021.08A ; V 3185.41A ; Cu 3273.97A ; Ag 3280.67A and Ti 3349.04A were used, a " density " figure from galvanometer deflexion less background deflexion being plotted against log concentration. The ash was digested with concentrated HNO_3 for 8 hours at 100°C., taken to standard volume, and 0.6 ml. filled into a graphite electrode 7.8 mm. in diameter with a boring 9.4 mm. deep and 4.7 mm. wide, previously burnt off in the arc for one minute after chemical purification. The solution in the electrode was dried for one hour at 110°C., then arced, as anode, at 9 amp. for one minute.

Brody and Ewing (1945) used an electrode with a centre post, which was made porous by previous arcing (10 amp., 50 volt, 7 sec.) before 0.1 ml. of solution was applied to it. Fe, Mn, Cu, Pb, Sn and Al were determined in food and faeces, the lines used being :

Sn	2840A	:	Bi	3024A
Pb	2833	:	Bi	3024
Mn	2801.1	:	Bi	2898
Fe	3020.6	:	Bi	2898
Al	3082	:	Bi	2898
Cu	3274	:	Bi	2898

with Bi as internal standard. The analytical arc was 7 amp. at 30-35 volts for 30 seconds, but the polarity is not indicated. The effects of certain extraneous elements such as Na and K on the intensity ratios are discussed and suitable buffer solutions for the solution of the ash to counteract such effects are given. An accuracy of $\pm 10\%$ for single and $\pm 5\%$ for triplicate determinations was obtained.

Methods worked out for the analysis of certain ceramic materials should be directly applicable to the analysis of soils. Smith and Hoagbin (1946), dealing with the analysis of Al_2O_3 used in ceramics for the presence of Na, Si, Ga, Pb, Sn, Fe, B and K have used a 10 amp. d.c. arc controlled by resistance and choke. The material was packed into a cavity $\frac{5}{64}''$ deep and $\frac{7}{32}''$ diameter in a $\frac{1}{4}''$ carbon electrode. The internal standard was mixed with carbon and combined with the sample in the ratio 1 carbon : 2 sample by shaking up to 1 g. in a 1 oz. screw capped square glass bottle containing eight $\frac{1}{4}''$ steel balls. Hand shaking for one minute was superior to mechanical shaking for one hour. The arc was burnt for 30 seconds at 0.2″ separation with the sample in the anode. Quantitative analysis for Na and Si used the following lines :

Na	3302.3A	:	Li	3232.6A
Si	2532.3	:	Cr	2557.1
Si	2438.7	:	Mn	2430.3

log intensity ratios being obtained from a stepped Fe plate calibration curve. Average deviations of 3.5 and 4.0% were obtained for Na and Si respectively. Jaycox (1947) has described the determination of Al, B, Ba, Be, Ca, Cr, Fe, Li, Mg, Mn, Na, Pb, Si, Ti, Zn and Zr in ceramic and similar materials in a 10 amp. d. c. arc, one part of the sample being diluted with 19 parts of CuO and 40 of carbon powder and filled into a crater in a graphite electrode.

Ahrens (1945 a), for the determination of trace elements in clays, mostly on a semi-quantitative basis, used a carbon anode of 5 mm. diameter with a boring 4.5 mm. deep and 3.0 mm. diameter, and a pointed cathode. With a wide electrode to carry the sample, a pointed counter electrode helps to stabilize the arc during its initial stages. For 20 seconds the arc was run at 2.5 amp. then increased to the maximum available (6.5 amp.) and successive exposures of 20 seconds made until the material had volatilized completely. Many workers report working at the maximum current available, illustrating the inadequacy of many d.c. arc sources supplied commercially for the type of problem encountered in the analysis of non-conducting powders. The preliminary arcing at 2.5 amp. was found advantageous for volatile elements such as Pb, Sn, Ga, Ag, Cd, Zn, whilst complete volatilization was necessary to obtain satisfactory results for Zr. An arc gap of 5 mm. was maintained. For quantitative analysis of Fe and W, Ahrens (1943 a, 1944) used a graphite anode 3.6 mm. in diameter with a boring 3.2 mm. deep and 2.8 mm. diameter, and gave a 30 second exposure. In his work on the determination of F by means of the CaF band in the arc, Ahrens (1942) employed a logarithmic sector for the quantitative estimation. This method of assessment has also been used by Wander and Brode (1941) for the determination of K in plant materials. Plant ash was mixed with an alumina-silicic acid flux and arced at 3.5 amp. for one minute, using added Cu as internal standard. K 4044.2A was compared with Cu 4022.7A.

For the determination of trace constituents (Li, V, Cr, Co, Ni, Cu, Zn, Sr, W and Au) in silicate rocks, P. H. Lundegårdh (1946 a) used a 4 amp. 110 volt arc with a 3.5 mm. electrode separation. The sample was in the cathode and the exposure lasted only 15 seconds, being started 5 seconds after the completion of the arc. The lines employed were Li 4602.0, 4602.9A; V 3183.96, 3184.00A; Cr 4254.34A; Co 3449.17A; Ni 3492.97A; Cu 3247.54, 3273.96A; Zn 3345.57A; Sr 4607.33A; Ba 4554.04A; W 4008.77A. Several interferences, such as W by Ti 4008.93A, are noted. Lundegårdh reports that of six spectrograms of a granite powder as few as two might be suitable for analysis using the line to background ratio photometric method following H. Lundegårdh. Similar lack of reproducibility is obvious from the photographs given by Smith and Hoagbin (1946). The author's experience has been that generally the use of an electrode with a boring which is wide in relation to its depth leads to lack of reproducibility due to wandering of the arc, spluttering and loss of material, and resultant variation of arc conditions following such effects. As a consequence, the cathode layer technique, involving the use of a thin electrode with a deep narrow cavity and a sample mixed with carbon powder, has been used practically exclusively at the Macaulay Institute. Before dealing with it, however, there are one or two modifications of the ordinary arc technique which should be mentioned.

Borovick (1943) has described an electrode in which the cavity is covered by a carbon lid having a single central opening. This is claimed to assist the gradual evaporation of volatile elements and to prevent ejection and spluttering. The analysis of soil and plant ash is facilitated. A similar electrode is illustrated by Churchill (1945), whilst the method has something in common with that of Preuss (1939) who fed the vapours of volatile constituents from a specially heated chamber holding 1 g. of sample into the arc through a hollow electrode.

An interesting development of the ordinary direct current arc is the high streaming velocity arc, in which the sample is packed into a recess in an electrode between a conducting central column and an insulated outer sleeve of graphite. When the sample is mixed with a suitable carrier, such as an ammonium salt or carbon powder, as much as 100 mg. of material can be brought into a 10 amp. arc in 4 seconds by this form of electrode, described by Hasler (1941) and Hasler and Harvey (1941). Fractional distillation effects are suppressed and good reproducibility is claimed. This electrode would appear to be of use for the determination of volatile elements such as Zn, Sn or Pb in biological materials. In view of the short exposure time a reproducible method of striking the arc is desirable, and Brockman and Hochgesang (1942) have described a suitable high frequency circuit which provides the initial discharge over the arc gap. A disadvantage of the high streaming velocity electrode is its complicated form, consisting of a steel base, graphite rod and sleeve and a "transite" insulator.

The method has been used by Austin and Bassett (1943) in the analysis of ceramic materials and by Standen (1944) for the qualitative analysis of trace constituents in a zinc matrix.

An adaptation of the Ramage spill technique to an arc source has been described by Thruston (1942) in the determination of Na, K, Ca, Mg, Mn, P and B in plant materials. A solution of the ash is evaporated on paper spills and fed into a horizontal 6 amp. d.c. arc between Cu electrodes 5 mm. apart. Errors were on an average less than 5%. A paper feed arc has also been used by Rusanov and Bodunkov (1940) for the determination of Ge in coal ash.

Chapter 6

ARC METHODS OF SPECTROGRAPHIC ANALYSIS

II. THE CATHODE LAYER ARC

a. General

The emission of light from an arc source is not uniform from all parts of the source. As has been mentioned, the anode is hotter and, as a consequence, it emits stronger continuous radiation and, with carbon electrodes, stronger CN bands. In order to avoid the excessive background blackening due to direct light from the anode, workers with the sample in the anode have generally either (a) prevented the direct light from the anode from reaching the prism, using only the light from the arc column, (b) used a very short arc or (c) added extraneous materials to the electrode to reduce the effect. A further factor, however, falls to be considered. The intensity of emission of spectral lines in the arc does not follow that of the continuous radiation and CN bands, but varies between anode and cathode depending on the properties (chiefly ionization potential) of the element or ion concerned.

Mannkopff and Peters (1931) drew attention to the usefulness, for analytical purposes, of the marked increase in emission which occurs with most elements in the neighbourhood of the hot tip of the cathode electrode. This effect, which is found whether the material is initially present in anode or cathode, is due, according to Mannkopff (1932), principally to increased concentration, and not to increased excitation, in a zone within one or two millimetres of the cathode, when the arc length is about 10 millimetres.

The cathode layer effect, as the enhancement has been called, is experienced chiefly with long arcs. The fact that lines due to impurities were most obvious in the cathode layer was first noticed by Fabry and Buisson (1910), but does not appear to have been applied in practice until it was taken up by Mannkopff and the Göttingen school under Goldschmidt.

The essential requirement of a method which takes advantage of the cathode layer effect is that only the light from the tip of the cathode and the neighbouring portion of the arc column should be employed. Generally one third up to one half of the column is allowed to contribute to the spectral image. Most workers with the cathode layer technique have followed Mannkopff and Peters in using a narrow cathode electrode with a deep narrow boring which gives a very steady arc with the discharge striking all round the lip of the crater continuously, and not moving from point to point as occurs with wider electrodes. Such electrodes hold 5-10 mg. of sample and burn away to the normal depth of boring (generally 8 mm.) in about 3 minutes. During this time the sample and electrode walls are consumed at the same rate, and the effect of the arc striking alternately to wall and sample should not be observed if the electrode is properly filled and a satisfactory ratio of carbon powder to sample is chosen for the material being analysed. With reversed polarity, the electrode burns away in less than a minute and the spectrogram obtained has a much darker background and weaker spectral lines of most elements. The increased emission in the neighbourhood of the cathode has been shown, even with the sample in the anode, by Hampton and Campbell (1944). Mannkopff and Peters (1931) found that only for Hg of the elements which they studied was the cathode layer enhancement very small. With Zn, Cu and Cd the increase in intensity was of the order of 5 to 10 fold, whilst for the elements of the first three columns of the periodic table, and for Si, Sn, Pb, Bi, Fe, Ni, Co and Sc it was even greater, the intensity in the cathode layer being sometimes up to 100 times that in the arc column. The effect is most obvious with small contents of the element in the electrode, when the lines may be visible only in the cathode layer. With larger amounts the emission from the arc column increases and the difference between it and the cathode layer decreases. The cathode layer effect is most obvious with elements of low ionization potential. It is explained by the migration of ions of the elements concerned to the cathode, where the neutral atom is re-formed and accumulates in the adjoining layer, the concentration of emitting neutral atoms being thus greater here than elsewhere. Ions of high ionization potential, such as B, which are scarcely ionized in the arc, do not show an appreciable cathode layer effect. The migration of ions to the cathode also explains the enhancement of lines of ionized atoms, the so-called spark lines, in the neighbourhood of the cathode.

The cathode layer arc has been extensively used, particularly for the analysis of rocks, minerals and soils, both for semi-quantitative and quantitative work, and these applications will be dealt with in turn.

b. Semi-quantitative Analysis in the Cathode Layer Arc

To take full advantage of the increased sensitivity given by the cathode layer emission, it is necessary to produce an image of the source at the slit of the spectrograph. At the Macaulay Institute this has been done by means of a Hilger F292 or F997 spherocylindrical lens, with its cylinder axis vertical, projecting a 20 mm. long image of a 10 mm. arc onto the plane of the slit of a Hilger Large Quartz spectrograph. 2 mm. of the image of the cathode tip and 7 mm. of the arc column image fall on the slit which is 9 mm. long and 0.01 mm. wide. The image of the anode thus falls 13 mm. below the slit and no light from it enters the spectrograph. The arc is controlled as already described (see p. 55) and is run at a current of 9 amp. The sample to be analysed is mixed, unless where otherwise indicated, with an equal amount of pure carbon powder. The electrode is made from pure carbon rod, 5 mm. in diameter, 25 mm. long and reduced in diameter over the upper 15 mm. to 2.8 mm. The boring is 0.8 mm. ($\frac{1}{32}$ inch) in diameter and 8 mm. deep. The anode is a portion of the same rod about 25 mm. long and 5 mm. in diameter. It need not have specially machined ends, portions as broken off can be used.

The electrodes are approximately aligned in the arc stand, with the shutter open, then the anode is brought into contact with the cathode with sufficient resistance in circuit to give a current of 2-3 amp. This current is obtained through the sliding resistance. The spot of light obtained when the electrodes touch allows the cathode tip to be sent to its proper position by the image on the rear screen (see p. 58). After a few seconds, the anode is separated from the cathode and the arc length increased to 10 mm. The current is increased at the same time to 9 amp. by means of the tapped resistance, with final adjustment on the sliding resistance. The speed of separation and increase of current are controlled by the sound and appearance of the arc, but should not take more than 5 seconds. During the exposure, the burning away of the anode and cathode is observed on the rear screen and the electrodes are adjusted individually so that the arc length and position are kept constant.

Fifty-five seconds after the separation of the electrodes, the shutter is closed for five seconds while the plate holder is racked to a new position. With a 9 mm. slit, these spectrograms can be taken 10 mm. apart. Three such exposures are given for each sample and 9 spectrograms, covering 3 samples, can be carried on one plate. A convenient automatic shutter can be made from a disk with a 30° cut-off in front of the slit, driven by a Sangano Weston synchronous motor giving one revolution in 60 seconds. A contact on the disk can be arranged to operate a buzzer as the cut-off comes in front of the slit, indicating when the plate should be racked to its new position. At the beginning of an exposure the disk is set with the shutter just clear of the slit, and the motor is started immediately the arc is in full operation. In practice a device of this type has proved very useful, as it enables full attention to be given to the control of arc position and current.

The exposure period in qualitative and semi-quantitative work is broken up into three separate spectrograms because, as has been noted, the nature of the line image obtained and its time-intensity relationship may give valuable information regarding the element responsible for the line. Thus, to give two simple examples, the Zn doublet at 3302.6, 3302.9A cannot be confused with the Na doublet 3302.3, 3303.0A under such conditions even on the most casual inspection, as the Na doublet shows a pronounced cathode layer effect whilst Zn does not, whilst Zn is very volatile, with its strongest intensity in the first spectrogram, and Na persists into the second spectrogram to a greater extent. Similarly the volatility difference should allow one to distinguish between the volatile Sn 2839.99A and the weak Cr line at 2840.02A. Confirmation of possible Cr interference is then obtained by inspection of stronger Cr lines.

In the examination of soils about 0.5 g. of ground material (see Chapter 11) is first ignited at 450°C. as it has been found that although most soil powders can be arced without previous ignition, occasional exceptions occur where the presence of organic matter suppresses the emission of lines. From this stage the treatment of soils, ashed plant materials, rocks and minerals, or standard mixtures is similar when a qualitative or semi-quantitative examination is the object.

20-30 mg. of material are weighed out on glazed paper (2 cm. × 2 cm.) on a 500 mg. Oertling torsion balance and mixed in a small agate mortar with its own weight of carbon powder (obtained by grinding purified carbon rods in an agate mortar). Some of the mixture is then returned to glazed paper and 7-8 mg. filled into an electrode (8 mm. × 0.8 mm. boring). To do this, the electrode is mounted in a small wooden block and a tight fitting paper collar slipped over the narrow portion, its length being such that it projects 1 mm. above the top of the electrode. A little of the mixture is poured into this collar and introduced into the boring by tapping the electrode block gently. The mixture is compressed in the boring with a blunt needle which just fits the cavity, and the process continued until the boring is completely filled. The introduction of powder to the cavity and its compression should be done in small amounts. If too much is put in at once the packing may become uneven and part of the sample is then liable to jump out at the beginning of the exposure. Some workers have recommended the use of a little carbon powder to complete the filling, but this has not been our practice. Electrodes can be filled easily and expeditiously provided the work bench is well lighted.

The utmost possible cleanliness and choice of materials which are not liable to cause contamination are essential at every stage. Especial care must be taken to ensure that the agate mortar is clean. This can generally be achieved by grinding out with finely powdered alumina or silica or with the next sample to be filled, after a preliminary cleaning with cloth or cotton wool. The mortar should be washed with acid to clean the surface after

each set of electrodes is filled. If one sample is subsequently found to contain an abnormally high content of any constituent which is being determined, the sample filled immediately following it should be repeated to check up on the possibility of contamination. An agate mortar which becomes contaminated with a particular trace constituent is occasionally found, Strock (1936 a) reporting one which could not be cleaned after becoming contaminated with Li.

For qualitative work a marked plate carrying a spectrogram of the trace constituents which are to be looked for, in any suitable silicate base, such as is provided by town refuse dust (see p. 65) is adequate for soil samples, whilst a similar plate with a matrix of alkalis, alkaline earths and phosphate is useful for work with plant ash. When semi-quantitative estimations are being made, the procedure is to employ a series of standard mixtures which contain the major constituents in amounts as close as possible to those normally occurring in the sample being analysed, and the trace constituents in incremental amounts varying usually from 1 p.p.m. to 1 per cent.

A suitable soil base has been prepared by mixing together in an agate mortar specially purified samples of SiO_2 63%, Al_2O_3 20%, Fe_2O_3 5%, CaO 2%, MgO 2%, Na_2CO_3 3.5%, K_2SO_4 3.5%, TiO_2 1%, and sintering overnight in an electric furnace at 1250°C. This material, after grinding to a fine powder in an agate mortar, was used for the preparation of standard dilutions of the trace constituents. The constituents were purified as described in Chapter 11.

In order to avoid weighing out small amounts of the trace constituents it has been found convenient to prepare a series of trace element mixtures each containing from 5 to 10 elements. Four groups which have been prepared are as follows ; other suitable combinations are of course possible :

Standard Mixture	A		B		C		D	
LiF	0.3738 g.	Co_3O_4	0.1362 g.	SnO_2	0.1270 g.	As_2O_3	0.1321 g.
RbCl	0.1414	NiO	0.1272	PbO	0.1077	Sb_2O_3	0.1197
CsCl	0.1266	CuO	0.1252	Tl_2O_3	0.1116	SeO_2	0.1403
BaO	0.1117	MoO_3	0.1500	ThO_3	0.1138	TeO_2	0.1251
SrO	0.1182	$K_2Cr_2O_7$	0.2824	ZnO	0.1245	BeO	0.2773
CeO_2	0.1228	Ag_2O	0.1074	CdO	0.1142	HgO	0.1080
H_2WO_4	0.1350	V_2O_5	0.1784	Bi_2O_3	0.1114	GeO_2	0.1441
TiO_2	0.1666	ZrO_2	0.1351	Ga_2O_3	0.1344		
Mn_2O_3	0.1436	Y_2O_3	0.1271				
		La_2O_3	0.1173				
	1.4406		1.4863		0.9446		1.0466

The summation weight of each mixture contains 0.100 g. of the individual elements. Other elements which were not available when the

mixtures were prepared but which might be included are Sc, In and Ta, whilst B should be considered if B-free carbons are being used.

To prepare the strongest standard the necessary amounts of each trace element mixture (one tenth of the summation weight if 1 g. of standard is being made) and the amount of the base mixture required to give a 1% content of each trace constituent in the whole are ground together for 15 minutes by hand in a small agate mortar. From this 1% standard, subsequent dilutions are made in steps of 1 : 0.316, 0.316 g. of the mixture being ground for 15 minutes with 0.684 g. of base. By this means a series of nine mixtures containing each individual trace constituent in amounts of 1%, 0.316%, 0.1%, 0.0316%, 0.01%, 0.0032%, 0.001%, 0.00032% and 0.0001%, that is from 10,000 down to 1 p.p.m., is prepared. The sensitivity of the various trace constituents in this base is given in Table 3.

It must be noted that the stronger standards do not contain the full percentage content of the major constituents, and if any of these is subsequently to be used as an internal standard in quantitative work it should be added in sufficient amount to the first standard mixture to bring its content up to the required value. Scott (1945) has given a simple means of calculating the required addition of the internal standard constituent. If a=total weight in grams of the compound (e.g., Fe_2O_3) containing the internal standard which must be present in one gram of mixture, and b=total weight (in grams) of the trace element compounds added, then x=weight (in grams) of the base (containing a g. of Fe_2O_3 per g.) which it is required to take and $(1-b-x)$ is the weight of the extra Fe_2O_3 necessary ; x being given by

$$x = (1 - a - b)/(1 - a) \text{ g.}$$

In the above, if 5% Fe_2O_3 is required,

$$\begin{aligned} a &= 0.0500 \text{ g. } Fe_2O_3 \\ b &= 0.1441 + 0.1486 + 0.0945 + 0.1047 \\ &= 0.4919 \text{ g.} \\ x &= (1 - 0.050 - 0.492)/(1 - 0.050) \\ &= 0.458/0.950 \\ &= 0.482 \text{ g.} \end{aligned}$$

Extra Fe_2O_3 required $= 1 - 0.482 - 0.492$

$= 0.036$ g.

Thus, to prepare a 1% mixture of the above elements with 5% of Fe_2O_3 present, one takes 0.483 g. of base, 0.492 g. of trace element mixtures and 0.036 g. of Fe_2O_3.

For semi-quantitative analysis of ashed plant materials the base material must be similar in composition to the ash in order to obtain

satisfactory results, owing to the effect of major constituents on the line intensity of the trace constituents. Ashes of different parts of plant species vary considerably in composition, but a mean value for pasture herbage approximates to

K_2O	30%	P_2O_5	10%
Na_2O	5%	SO_3	10%
CaO	10%	CO_2	10%
MgO	5%	Fe_2O_3	0.2%
SiO_2	20%	Al_2O_3	0.3%

and a suitable base can be prepared from KH_2PO_4, K_2SO_4, K_2CO_3, MgO, SiO_2, Na_2CO_3, $CaCO_3$, Fe_2O_3 and Al_2O_3.

Scott (1941 b) records the minimum sensitivity of the various trace constituents in this type of base, and his data are given in Table 3. This Table also includes data obtained by the author for many of the same elements in a $CaCO_3$ base used for the estimation of trace constituents in limestones.

For the preparation of standards for the semi-quantitative examination of plant ashes, it is possible to reduce the required number of dilutions to 6 and at the same time cover the range of contents likely to be encountered in plants. Only certain of the elements in Table 3 are observed directly in plant ash, and a suitable standard series would contain

Ba	31.6 — 10,000 p.p.m.
Sr	31.6 — 10,000
Rb	31.6 — 10,000
Mn	31.6 — 10,000
Zn	31.6 — 10,000
Cu	10 — 3,162
Mo	3 — 1,000
Sn	3 — 1,000
Pb	3 — 1,000
V	3 — 1,000
Ti	3 — 1,000
Co	1 — 316
Ni	1 — 316
Cr	1 — 316

In a normal plant, the ash content is generally some 3-12% of the oven dry matter, in a clean mixed pasture herbage the usual value being from 5 to 8%. The above ranges thus cover the normal dry matter contents of trace constituents reported in the literature, except possibly for some abnormally high Mn and Zn contents and for contents which are in any case too low to be observed spectrographically.

TABLE 3

Wavelength and Approximate Sensitivity of Convenient Analysis Lines of Trace Constituents in Soil, Plant Ash and $CaCO_3$ Bases in the Cathode Layer Arc

Element	Wavelength	Minimum sensitivity in p.p.m.			Element	Wavelength	Minimum sensitivity in p.p.m.		
		Soil	Plant Ash	$CaCO_3$			Soil	Plant Ash	$CaCO_3$
Ag	3280.7	1	1	2	Mn	4034.5	10	10	—
As	2349.8	1000	1000	—	Mo	3170.3	1	10	5
Ba	4934.1	5	3	5	Ni	3414.8	2	3	5
Be	3130.4	5	30	5	Pb	2833.1	10	30	10
Bi	3067.7	100	100	10	Rb	7800.2	20	5	30
Cd	3261.1	300	1000	200	Sb	2877.9	300	100	—
Ce	4222.6	500	1000	—	Sc	4246.8	10	—	—
Co	3453.5	2	3	5	Sn	2840.0	5	30	10
Cr	4254.3	1	3	2	Sr	4607.3	10	10	10
Cs	8079.0	300	—	—	Ti	3989.8	—	10	—
Cu	3247.5	1	1	1	Tl	2767.9	50	30	10
Ga	2943.6	1	10	3	V	4379.2	5	3	10
Ge	2651.2	10	30	10	W	2947.0	300	1000	—
Hg	2536.5	1000	10,000	—	Y	3327.9	30	10	20
La	3337.5	30	20	25	Zn	3345.0	300	3000	1000
Li	6707.8	1	1	1	Zr	3392.0	10	30	10

To carry out a semi-quantitative analysis, spectrograms of the series of standard mixtures are recorded on plates which are compared in a Hilger Judd Lewis comparator with those for the unknown samples prepared in the same way. With a Hilger Large Quartz Spectrograph the whole spectrum cannot be carried on one plate. Generally two plates covering the ranges 2480-3500A and 3300-8500A are adequate, but a third plate covering the region below 2500A may be required if, for instance, As or Be is of particular interest. Ilford Chromatic plates, developed for $2\frac{1}{2}$ minutes at 18°C. in Ilford I.D.2 metol-hydroquinone developer, are used for the ultra-violet regions and Ilford Long Range Spectrum plates, developed for $4\frac{1}{2}$ minutes in the same developer, for the longer wavelength region. The sensitivities quoted in the above tables are liable, particularly in the infra-red regions, to vary with the different batches and ages of plate. In order to obtain optimum sensitivity, the spectrograph itself must be in good adjustment with crisp definition of weak lines.

When standard plates are inspected in the Judd Lewis comparator it is easily possible to distinguish between the densities of adjoining dilutions which vary by approximately 3-fold, and, with practice, good interpolations can be made to an accuracy of $\pm 30\%$ of the actual amount present, especially for contents at which the line is not too dense. For contents near the sensitivity limit quite accurate results are obtainable. The method

suffers because the assessment is subjective, and some observers are much more proficient than others. When this is kept in mind, and the size of the possible error realized, the method can serve a useful purpose in the examination of soils, plant ashes, rocks, minerals and fertilizers, particularly in the detection of excesses or in eliminating the possibility of deficiencies where the content of the element found is above normal. The semi-quantitative cathode layer method has been used at the Macaulay Institute chiefly for the analysis of rocks and minerals—the materials from which soils are derived—in a series of geochemical investigations into the distribution of trace constituents in different rock types. This was the purpose for which the method was initially worked out, and it was used in Göttingen by Goldschmidt and his collaborators. Goldschmidt and Peters (1931 a) found Ga 2943.6A visible down to 5 p.p.m. of Ga_2O_3. The line at 2874.2A was equally sensitive but coincided with an Fe line. For Sc, Goldschmidt and Peters (1931 b) used the lines 3359.69A and 3613.83A, obtaining a similar sensitivity for Sc_2O_3 as for Ga_2O_3. Zr and W are liable to interfere. For Y_2O_3 the lines at 3600.73, 3633.13 and 3710.30A were all visible below 10 p.p.m. The sensitivity found by Goldschmidt and Peters (1932 a) for Be, namely 10 p.p.m. of BeO for the 2348.62A line, is somewhat lower than generally found. The precious metals (1932 b) and boron (1932 c, d) are dealt with in further papers. The Ge lines at 3039.08A and 2651.15A were both observed to below 10 p.p.m. of GeO_2 (Goldschmidt and Peters, 1933 a) whilst further work dealt with Cr, Ni and Sn in meteorites (1933 b), trace elements in coal (1933 c) and As (1934). Goldschmidt, Berman, Hauptmann and Peters (1933) and Goldschmidt, Bauer and Witte (1934) have dealt with the alkali metals. Ernest and Hörmann (1936) have determined V, Ni and Mo in sea water, after a preliminary chemical concentration. Noll (1934) and Engelhardt (1936) have used the method for Sr and Ba, respectively, in rocks.

Tongeren (1938) has given a full and detailed account of his use of the semi-quantitative cathode layer arc technique. The spectrograph employed was a Mannkopff (1931) type two prism glass spectrograph covering the wavelength range 3600-5000A only. The preparation of standard mixtures and dilution series followed that already described. The electrodes were prepared from commercial grade cinema carbons by prolonged treatment with aqua regia (for some weeks) followed by leaching (during 3-4 months) with HCl of gradually decreasing concentration and finally with acidified distilled water. Ca, Al and Fe were still present in some quantity. Amounts of Sr, Ba, Ti, Cr and Mn were too low to affect results for the types of material (rocks and minerals) examined. The electrodes used were 5 mm. diameter with a boring in the cathode 4 mm. deep and 1.1 mm. wide, to take 9 ± 1 mg. of a normal rock sample. The mains supply was 230 volt d.c. and for each sample seven 30 second exposures were made with incremental currents as follows : 30 sec. at 2-3 amp., 30 sec. at 5 amp., 30 sec. at 7 amp., and 4×30 sec. at 9 amp. On each plate was included one series of exposures of the sample alone and one with an admixture of Na_2CO_3. Carbon powder

was not employed. The elements Ag, Al, Ba, Ca, Cd, Ce, Co, Cr, Cs, Dy, Er, Eu, Fe, Ga, Gd, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Sc, Si, Sm, Sn, Sr, Tb, Th, Ti, Tl, V, W, Y, Yb, Zn and Zr are discussed individually, spectrograms of all concentrations from 1% to 1 p.p.m. in an SiO_2 base in the presence and absence of 50% Na_2CO_3 being described in practically every case, with tables of lines visible at the different contents. Tongeren has made a most useful contribution in this account of the analysis of rocks, and the method is directly applicable to soil work. The restricted wavelength range covered is, however, unfortunate : somewhat similar information covering shorter wavelengths has been given by Eeckhout (1945 b). The discussion by Tongeren of those trace elements, such as many of the rare earths, whose best lines are in the 3600-5000A range, is of particular interest. The usefulness of a spectrograph with a greater dispersion than that given by the Littrow type large quartz spectrograph for these wavelengths is emphasized in the discussion of possible interference.

Analyses of rocks and minerals and plant ashes by the cathode layer technique are reported by Rankama (1939, 1940). Rost (1939) has used it to study sulphide ores, particularly for Co and Ni. Oftedal (1940) used a Mannkopff type quartz spectrograph to investigate the trace constituents of Norwegian sulphide ores. His electrodes had cavities 4×1.5 or 4×1 mm. and were burnt at 5A for up to 2-2½ minutes for complete combustion. Admixture with an equal amount of carbon powder was necessary with iron-rich sulphides to prevent spluttering. Visual comparison, with the above steps in the standard dilution series, was accurate to ×2 or ×3. The elements discussed, for which wavelengths and sensitivities are given, were Cu, Ag, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, Mn, Fe, Co. The effect of different base materials, naturally occurring or artificially produced, is considered. The synthetic standards often showed lines weaker than those given by natural materials with the same content, especially for the more volatile constituents. This is probably due to the form of combination of the volatile constituents in the material being examined, and the speed with which they entered the arc column.

c. Quantitative Analysis in the Cathode Layer Arc

The quantitative method adopted at the Macaulay Institute for the determination of most trace constituents involves excitation in the cathode layer arc, followed by photometric determination by the variable internal standard method (see pp. 22, 28) (Davidson and Mitchell, 1940 a). The electrode preparation follows exactly that already described for the semi-quantitative method, whilst the optical system involves the imaging of the arc at the collimator by means of a spherical quartz lens (Hilger F1025, F1083 or H438 for the large quartz spectrograph) at the slit, with a rotating step sector between lens and slit. By means of a mask at the collimator which cuts off the lower half of the prism, only the light from the cathode tip and the adjoining portion of the arc column is employed. For initial adjustment the slit is opened wide and the position of the arc image observed

on a screen at the collimator. The position of the arc is so arranged that only about 1 mm. of the image of the cathode tip is unmasked, whilst the anode image is well below the level of the mask. This position is marked on the rear screen, so that it can be maintained when the arc is in operation.

The arc is made, as described above, by bringing the electrodes together, positioning the cathode from the spot of light momentarily obtained, allowing the current to flow through the closed electrodes for a few seconds at 3 amp., then separating them, at a speed depending on the noise and appearance of the arc, to 10 mm. and increasing the current simultaneously to 9 amp. Each exposure is made with a six-step sector, running at a constant speed between 250 and 500 r.p.m., in order to obtain blackening curves for each line.

The exposure is continued until the sample is completely consumed, as indicated by the arc column assuming the violet coloration typical of the CN bands. With 2.8 mm. diameter carbon electrodes 8 mm. deep, this takes about 3 minutes. The wavelength range found most generally useful is 2800 to 5000A, which covers sensitive lines of most trace constituents. Ilford Chromatic Plates are employed, being developed for $2\frac{1}{2}$ minutes at 18°C in Ilford I.D.2 metol-hydroquinone developer, then fixed, washed and dried at room temperature.

The method of measurement of the plate has already been described—the variable internal standard, background corrected, constant density method (see p. 28) being employed for Co, whilst the same method without background correction is generally adequate for other trace constituents, but background corrected working curves have been prepared for most trace constituents.

For the preparation of working curves, standard mixtures, prepared as described earlier (p. 81), are employed, it being essential to ensure constant content of the internal standard. The quantitative method has been employed in the main in conjunction with the concentration procedure described in Chapter 11, which provides a precipitate of the trace constituents in a matrix of Al_2O_3, with Fe_2O_3 as internal standard. Dilution series have therefore been prepared containing the trace constituents in a matrix of Al_2O_3, with Fe_2O_3 as internal standard. The range of Fe_2O_3 generally covered is from 2 to 25% Fe_2O_3 in 8 dilution series, but for certain elements the effect of change of the internal standard content has been studied up to 100% Fe_2O_3 (Scott, 1946).

The lines which are employed in the quantitative method are detailed in Table 4, which is taken largely from Scott (1945, 1946). The table includes line configurations for the trace elements and also for the iron lines used as internal standards. The sensitivity of the quantitative method is not quite so great as that of the semi-quantitative, the lower limit of visibility being about 3 times that of the latter. Whilst Co can be detected semi-quantitatively at about 2 p.p.m. photometric measurement is first practicable about 10 p.p.m. and visual detection in the strongest step is possible only above 5 p.p.m. with our E 1 spectrograph.

Table 4

Wavelengths, Classifications and Useful Ranges of Lines of Trace Elements and Internal Standards used for Quantitative Analysis by the Cathode Layer Arc Technique in an Alumina Matrix

Trace Elements				Internal Standards				Useful Range
Element	Wave-length	High term	Low term	Element	Wave-length	High term	Low term	
V	4379.24	$^6F_{5\frac{1}{2}}^0$	$^6D_{4\frac{1}{2}}$	Fe	4250.79	$z^3G_3^0$	a^3F_3	10—3000 p.p.m.
Cr	4254.35	$z^7P_4^0$	a^7S_3	Fe	4250.79	$z^3G_3^0$	a^3F_3	3—3000 p.p.m.
Co	3453.51	$y^4G_{5\frac{1}{2}}^0$	$a^4F_{4\frac{1}{2}}$	Fe	3451.92	$u^5D_2^0$	a^5P_1	10—3000 p.p.m.
Ni	3414.77	$^3F_4^0$	$^3D_3$	Fe	3413.14	$w^5D_3^0$	a^5P_2	10—3000 p.p.m.
Zn	3345.02	$^3D_3$	$^3P_2^0$	Cd	3261.06	$^3P_1^0$	$^1S_0$	0.1—10%
Zn	3345.02	$^3D_3$	$^3P_2^0$	Fe	3305.97	$v^5P_3^0$	a^5P_2	0.1—10%
Ag	3280.68	$^2P_{1\frac{1}{2}}^0$	$^2S_{\frac{1}{2}}$	Fe	3305.97	$v^5P_3^0$	a^5P_2	3—1000 p.p.m.
Cu	3273.96	$^2P_{\frac{1}{2}}^0$	$^2S_{\frac{1}{2}}$	Fe	3305.97	$v^5P_3^0$	a^5P_2	3—1000 p.p.m.
V	3185.40	$^4G_{5\frac{1}{2}}^0$	$^4F_{4\frac{1}{2}}$	Fe	3196.93	e^7F_5	$z^7D_4^0$	10—3000 p.p.m.
Sn	3175.02	$^3P_2$	$^3P_1^0$	Fe	3196.93	e^7F_5	$z^7D_4^0$	100—3000 p.p.m.
Mo	3170.35	$y^7P_3^0$	a^7S_3	Fe	3196.93	e^7F_5	$z^7D_4^0$	10—3000 p.p.m.
Be II	3130.42	$^2P_{1\frac{1}{2}}^0$	$^2S_{\frac{1}{2}}$	Fe	3116.63	$x^5D_2^0$	a^5F_1	30—3000 p.p.m.
Ge	3039.06	$^1P_1^0$	$^1D_2$	Fe	3116.63	$x^5D_2^0$	a^5F_1	100—3000 p.p.m.
Ga	2943.64	$^2D_{2\frac{1}{2}}$	$^2P_{1\frac{1}{2}}^0$	Fe	2929.01	$y^5F_2^0$	a^5D_3	10—3000 p.p.m.
Sn	2839.99	$^3P_2^0$	$^3P_2$	Fe	2838.12	$y^5G_2^0$	a^5F_2	30—3000 p.p.m.
Pb	2833.07	$^3P_1^0$	$^3P_0$	Fe	2838.12	$y^5G_2^0$	a^5F_2	100—3000 p.p.m.
Tl	2767.88	$^2P_{\frac{1}{2}}^0$	$^2D_{1\frac{1}{2}}$	Fe	2767.52	$w^5D_4^0$	a^5F_4	100—3000 p.p.m.

Preuss (1935) has described quantitative and semi-quantitative methods for the determination of trace constituents in tektites. The lines suggested as suitable are Li 3232.7A ; Rb 4201.8A ; Cs 4555.3A ; (these only in alkali extracts because of Fe, Na and Ti interference—Goldschmidt, Berman, Hauptmann and Peters, 1933) Be 2348.6A ; Sr 4077.7, 4215.5, 4607.3A ; Ba 4554.0, 4934.1A ; Zr 2571.4, 3392.0, 3438.2A ; Hf 2638.7, 2773.4A ; V 2924.0, 3102.3, 3183.4, 3184.0, 3185.4A ; Cr 2677.2, 4254.3A ; Mo 3170.3A ; W 2947.0A ; Mn 2576.1, 2798.3, 2801.1A ; Co 2407.3, 3405.1, 3453.5A ; Ni 3414.8, 3050.8A ; Cu 3247.5, 3274.0A ; Ag 3280.7, 3382.9A ; Au 2676.0A ; Zn 3345.0, 3345.5A ; Cd 2288.03A ; Hg 2536.5A ; Ga 2943.6A ; In 3256.1, 3039.3A ; Tl 2767.9A ; Ge 2651.1A ; Sn 2840.0A ; Pb 2833.1A ; As 2349.8A ; Sb 2598.1A ; Bi 3067.7A ; Te 2385.8A. These lines, except possibly for the alkalis, where the lines in the red are more sensitive and less liable to coincidence, are those which are most often used for the elements in question. Preuss (1935) also gives details of different methods of photometry, electrode purification and sources of suitable chemicals for standard mixtures. Preuss (1938) deals in more detail with photometry and relationship of line intensity to the amount present in the electrode, giving a method for correction for spectral background. Preuss used the usual cathode layer electrode, with a boring 8 mm. deep and 1 mm.

diameter in a 2.8 mm. diameter carbon. A 1 : 1 carbon powder mixture was employed and a long 10 mm. arc used, the exact length having no marked influence on the accuracy.

Strock (1936 a, b) has described in detail the technique of quantitative analysis using the cathode layer arc, illustrating it by the determination of Li with Sr as internal standard. Curves illustrating the increase in self reversal at a given percentage content with increasing amounts of sample, and thus of absolute amounts of Li, in the electrode, are of interest in showing that for lines which end in a stable electron level the minimum of material should be employed. Using Sr 6408.5A as internal standard, Li 6707.9A is much more liable to show reversal than Li 6103.6A. Bauer (1935) used the cathode layer technique, finding it the most suitable method for the determination of La with Zr as internal standard. Using electrodes 2.5 mm. in diameter with a 4.0 × 0.7 mm. boring at 8 to 10 amp., the sensitivity was 0.001% La_2O_3 in Al_2O_3 and 0.0025% La_2O_3 in CaO. Kvalheim and Strock (1939) used an electrode with a 1.5 × 4 mm. bore for their determination of Sc in igneous rocks, with La as internal standard. These shallower electrodes are employed where the constituent being determined is relatively involatile, and are of use in such cases, just as a boring up to 12 or 15 mm. deep may be advantageous when a very volatile constituent such as Zn is being determined. Generally, however, when several constituents are being determined simultaneously, a compromise must be chosen, and the most useful depth would appear to be that already given, namely 8 mm. Similarly, the sample may be burnt alone, mixed with carbon powder or with sodium chloride, or with a mixture of both, in varying ratios depending on the exact object of the determination. A 1 : 1 carbon mixture is most generally useful although more carbon may be required with certain types of material to give a steady burn. Rankama and Joensuu (1946) use one part of the sample, 4 of carbon and one of NaCl for titaniferous minerals, in order to avoid spluttering. The addition of NaCl, or other spectroscopic buffer, helps to reduce the effect of variation in the composition of the samples compared with the standard, but may at the same time reduce the intensity of trace constituents. Our experience is that Zn in particular is greatly depressed by NaCl.

The problem of the choice of a suitable internal standard for any element is complex. An ideal internal standard would behave similarly to the analysis line under all possible types of variation which could occur in the source. The factors which come into play are arc current and voltage, electrode separation, amount of material in the arc and the effects of a loss of material in bulk from the arc as a result of a splutter. The difficulty is increased by the very restricted choice of elements available when it is desired to determine simultaneously as many constituents as possible. The most suitable internal standard for a particular constituent is often an element which is itself to be determined. An internal standard can be either an element absent from the original material but added in known amount, a constituent present in such overwhelming excess over the other

constituents that its amount can be considered invariable (as Fe in steels), or a constituent present in moderate, variable, but known amount. It was for the last case that the variable internal standard technique was developed at the Macaulay Institute, as Fe was present in, or could easily be added to, all samples analysed in amounts of the 2-20% Fe_2O_3 order. Fe has proved to be a reasonably good internal standard for such elements as Co, Ni, Mo, Cr, V and Ti, provided the effect of variation in matrix composition be eliminated. For Co and Ni, and in particular for Co, Fe is an excellent internal standard, the line pair Co 3453.51A : Fe 3451.92A having relative intensities which are scarcely affected by changes in the base in which they are determined (Scott, 1945) although their absolute intensities are appreciably altered by such changes.

For certain other of the elements determined, for instance Sn, Pb, and in particular Zn, Fe is not particularly satisfactory as an internal standard. The main difficulty under the conditions in the cathode layer arc would appear to be the greater volatility of these elements. If the arc burns uniformly and smoothly over the full period of the exposure the results are quite satisfactory, but if there be any loss of material as a result of a slight splutter when the arc is being made, then, although such elements as Co, Ni, Mo will be unaffected, the results obtained for Zn, Sn and Pb will be too high. This appears to be because, for a short period after a loss of material, the arc is practically a pure carbon arc, without the main matrix elements introduced, but with the more volatile trace constituents from the lower part of the boring being volatilized into it. Elements such as Zn, Sn, Pb appear to be much more sensitive in such an arc than they are in one loaded with Al or other elements from the matrix, hence high results are obtained. The tendency to splutter, which is present chiefly in certain concentrates of plant materials, can be practically eliminated by increasing the carbon : sample ratio to 2 : 1 and employing an electrode with a 1 mm. bore. In such conditions, with good filling of the electrode and experience in making the exposure, an unsatisfactory burn is uncommon. A method of indicating such a burn has, however, been introduced into the concentration method concerned (see p. 124). The most suitable internal standard for Zn is Cd, which is seldom present in plants and soils in detectable amounts (it has only been observed in one or two soils which had abnormally high Zn contents) so that it can be added to the material being analysed, in a content of from 0.5-2.0%, and Zn determined against both Fe and Cd. The Zn : Cd results are satisfactory even with bad burns, so that when Cd and Fe results agree a good burn is indicated, whilst in the event of disagreement, with the Fe results too high (it may be as much as 100%), the burn has been bad and the results for other volatile elements should also be rejected. The effect appears to be mainly that of volatility, so the method serves as a check on most elements intermediate in volatility between Cd and Fe. The more involatile constituents, in particular the rare earths and Zr, which have been found difficult by other workers, e.g., Strock (1941 b) and Strock and Drexler (1941) for Zr, have not so far been studied fully at the Macaulay

Institute. Scott (1945) has, however, pointed out the effect of base composition on the shape of the working curve for Zr, obtaining a normal curve with Na_2CO_3 and a curve with a flat maximum and subsequent fall for SiO_2.

For specific determinations, such as that of V, for which Cr is the most satisfactory standard (Kvalheim, 1941), it is possible to choose the best element available and so minimize the effects of changes in base composition as well as other effects. Strock (1936 a, b ; 1937) chose Sr for Li whilst Kvalheim and Strock (1939) employed La for Sc. Farmer (1946), at the Macaulay Institute, has been determining Cu in plant ashes with Ag as internal standard.

The choice of an internal standard is often restricted and the element, or the line of the element, most suitable on theoretical grounds, as far as our knowledge at present goes, frequently cannot be employed. In addition to factors limiting the elements from which the choice can be made, lines of suitable intensity, of a wavelength close to that of the element being determined, must be available. Physical properties and electronic configuration should correspond as closely as possible, and from the practical point of view the element should be easily determined if it is present, or easily incorporated in the required amount if it is to be added. At present, the criterion of the suitability of any internal standard is its effectiveness in practice. This would appear to be the chief justification for the use of Fe in the cathode layer method, with Cd as the further control element. The use of the spectral background as internal standard has been suggested by several workers (Borovick, 1942 ; P. H. Lundegårdh, 1946 a, b) for arc sources, in addition to its general employment in the Lundegårdh flame.

The effect of extraneous elements on the intensities of trace element lines and on the intensity ratios of analysis and internal standard lines has been studied by Scott (1945) in matrices consisting of some of the more important materials encountered in soil and plant work. Dilution series were prepared in Al_2O_3, SiO_2, $CaCO_3$, $Ca_3(PO_4)_2$, $Na_4P_2O_7$, NaCl and Na_2CO_3 for Co, Ni, V, Mo, Zr, Ag, Cu, Ga, Sn, Pb, Zn, Cd, Bi, La and Y. Most trace constituents gave their highest line intensities in the Al_2O_3 base. More volatile constituents, such as Cu, Ag, Zn, Bi and Cd, tended to be greatly depressed by NaCl, whilst Cr, V and Mo were enhanced by Ca salts and depressed by SiO_2. Using an Al_2O_3 matrix working curve, with Fe as the internal standard, results in a SiO_2 matrix were 50-90% less for these elements, whilst in $CaCO_3$ or $Ca_3(PO_4)_2$ they were a corresponding amount high. A similar effect between V and Fe is reported by Kvalheim (1941). Scott found that Co and Ni gave good results in all matrices except possibly SiO_2 which gave somewhat high values, although the absolute intensities of the lines varied appreciably, being low in sodium carbonate and phosphate. The results indicate the necessity of employing a working curve which has been obtained from standards in a base similar to the samples being analysed, or at least one whose reliability for the type of material being analysed has been established.

The literature on the effects of one constituent on the spectral line intensities of other constituents is much too extensive even to summarize briefly here. It is possible only to mention a few of the more important or relevant papers. Brode and Silverthorn (1939) have reviewed some of the earlier work and reach the conclusion that for complete quantitative analysis it is desirable for working curves to be prepared in which the extraneous elements are in equivalent quantity to that in the unknown series, and where some doubt exists as to their effect, a set of working curves should be prepared with different concentrations of the extraneous elements. Brode and Appleton (1940) and Brode and Hodge (1941) have carried this work further, the latter dealing with the effect of anions. Mandelstam (1938) suggested that the effect of large amounts of NaCl and KCl on the intensities of spectral lines of elements present in the carbon arc is due to the lowering of the temperature of the arc, as (Mandelstam, 1939 a) the addition of small amounts of NaCl reduces the arc temperature from about 7000°C. to 3000-4000°C. Subbaraya, Seshadri and Rao (1939 ; 1940 a, b ; 1941 ; 1942) and Subbaraya, Yusuff and Murthy (1942) have considered the effects of interaction of atomic energy levels in producing interference effects. Although these papers deal in particular with discharge tubes, the principles involved should be directly applicable to any type of source.

Difficulties arise in the determination of copper by the concentration method, because of contamination from reagents, but it has been found possible to determine it directly in plant ash. Oven dry plant material contains generally 2-20 p.p.m. of Cu, corresponding to 20-400 p.p.m. in the ash for ash contents of 5-10%. These contents are quite easily determined, provided one can overcome effects of variation in the matrix composition and also the effect of a slight Cu content which is often observed in the electrodes. The method adopted by Farmer (1946) in this laboratory is to mix one part of plant ash (from 1 g. of plant material ignited overnight at 450°C.) with one part of K_2SO_4 and 2 parts of carbon powder containing 500 p.p.m. of Ag, and to fill into carbon electrodes with a boring 4 mm. deep and 2.4 mm. ($\frac{3}{32}$″) wide in an electrode with an outer diameter of 3.85 mm.

The admixture of Ag, a suitable internal standard for Cu, is carried out by adding a solution of $AgNO_3$ to a quantity of carbon powder and, after heating to 400°C., mixing by thorough grinding in a mechanical agate mortar. The exact content of Ag is immaterial if all standards and unknowns are prepared from the same carbon powder, but 500 p.p.m. of Ag in the carbon is a suitable content. The different shape of electrode from normal was chosen, rather reluctantly, in order to increase the weight of sample relative to the amount of carbon burnt, so as to reduce the effect of traces of Cu in the electrodes. With the type of carbon rod employed, the effect has been reduced to less than 2 p.p.m. in the ash analysis, or to less than $\pm 2\%$ in a normal copper determination. After tests with various spectrographic buffers, K_2SO_4 was chosen as the most suitable for the purpose of

suppressing the effects of variation in the content of major constituents in the different types of plant ash.

The burn is not so steady as with the usual type of cathode layer electrode, but Farmer's results indicate satisfactory precision with a standard deviation for standards of ±5.5%. The Cu line at 3274.0A is measured, with Ag 3280.7A as internal standard, and logarithm of the relative intensities at D=0.4 plotted against log copper concentration. As the internal standard content is constant, no variable internal standard correction method is necessary. Background correction is essential because of variation in the Ca content of the samples.

Farmer has combined with this determination that of Ba, Sr, Mn and Mo in plant ash, with the Ca present in the ash (5-20% CaO) as variable internal standard. The lines employed, with the ranges in the ash that are covered are :

Ba	4934.1A	:	Ca	4878.1A	Ba	100 — 10,000 p.p.m.
Ba	4554.0	:	Ca	4581.4	Ba	30 — 1,000 p.p.m.
Sr	4607.3	:	Ca	4581.4	Sr	30 — 3,000 p.p.m.
Mn	4034.5	:	Ca	4098.6	Mn	100 — 10,000 p.p.m.
Mo	3170.3	:	Ca	3180.5	Mo	30 — 1,000 p.p.m.,

and the blackening curve separations read at a density of 0.5. For the last two elements the method has not proved particularly satisfactory so far, but determinations of Ba and Sr would appear to be adequate for purposes of surveying the trace element contents of plant materials.

Strock (1945) has studied the quantitative determination of Ni, Co, Mn, Cu, Pb, Sn, Sb, Ga, In, Tl, Ge, Ag and Hg in ZnS ores. Two sizes of cathodes, with bores of $\frac{7}{64}$" × 5 mm. (to take 60 mg.) and $\frac{1}{16}$" × 4 mm. (to take 10 mg.) were employed. The sample was mixed with 4 parts of carbon powder and one part of a mixture of 0.1% BeO in NaCl, Be 3130.4A being employed as internal standard. The lines employed, with the limits of detection in the large (L) and small (S) electrodes were :

Sb	2877.9A	— 500 p.p.m. (S)	
Bi	3067.7A	— 100 p.p.m. (S)	(Fe interferes)
Sn	2840.0A	— 5 p.p.m. (L)	100 p.p.m. (S)
Ge	2651.2A	— 50 p.p.m. (S)	
Ga	2943.6A	— 1 p.p.m. (L)	6 p.p.m. (S)
In	3039.4A	— 10 p.p.m. (L)	40 p.p.m. (S)
Ni	3414.8A	— 20 p.p.m.	
Co	3453.5A	— 20 p.p.m.	
Tl	not given	— 100 p.p.m.	
Hg	2536.5A	— 100 p.p.m.	(Co>0.2% interferes)

Blackening curve separation, involving the use of a step sector, was the method of photometry used.

Chapter 7

ARC METHODS OF SPECTROGRAPHIC ANALYSIS
III. INTERRUPTED AND ALTERNATING CURRENT ARCS

In addition to the normal direct current arcs which have been considered, there are several types of arc which employ an interrupted d.c. or an a.c. source. The initial object of the interrupted arc was to avoid overheating of the electrodes by the continuous d.c. arc, but experience has shown that for certain purposes an interrupted or a.c. arc may have other advantages. The high voltage a.c. arc in particular has been quite extensively used. An a.c. arc supplied through a resistance from mains at about 200 volts will run between bare carbon electrodes, but difficulties are experienced in maintaining the arc when the lower crater is charged with certain types of non-conducting powders. Such arcs are therefore generally supplemented with some form of high frequency carrier or activator current, which is also now employed to re-ignite the interrupted d.c. arc after each interruption.

a. The Interrupted Direct Current Arc

One disadvantage of the normal d.c. arc is that with metallic electrodes the current must be kept low enough to prevent melting of the electrodes. With 5 mm. Cu electrodes in a d.c. arc, currents above 4 amp. are difficult to maintain. It is possible to keep the electrodes cool by means of water-cooled jaws, but an interrupted d.c. arc is also effective. The use of a mechanical interrupter to make and break the arc circuit was described first by Gerlach and Ruthardt (1932). They produced 5 to 10 interruptions per second by means of a rotary switch, the arc being re-ignited each time by bringing the electrodes into contact. This involved a complicated arc stand with the upper electrode moved by means of a rotating cam. Grillet (1943) has described an upper electrode with a soft iron core, which is operated by a solenoid to make the arc after each interruption. The advantage of the Gerlach interrupted arc for the determination of As, Sb and Te was pointed out by Riedl (1932). McMillen and Scott (1937) used a vertical upper and horizontal lower rotating electrode.

Moving parts in the arc stand were eliminated by Pfeilsticker (1937, 1938) who superimposed on the low voltage arc circuit a high frequency discharge from a Tesla spark circuit. The d.c. discharge then takes place over the gap without the necessity of first bringing the electrodes together.

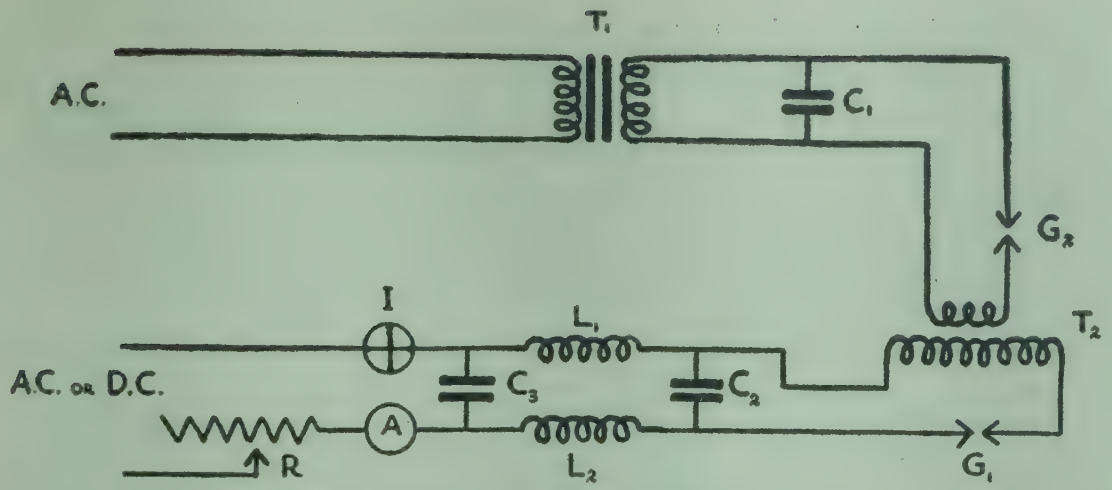

FIG. 23.—Circuit for an interrupted d.c. or a.c. arc
A—ammeter I—interrupter
C_1, C_2, C_3—condensers
G_1—analytical gap
G_2—auxiliary spark gap
T_1—transformer
T_2—Tesla transformer
L_1, L_2—H.F. chokes
R—variable resistance

A typical Pfeilsticker circuit is shown in Fig. 23 ; it is comprised essentially of 3 parts, the normal arc circuit with its usual controls and a mechanical interrupter, the Tesla spark circuit which superimposes the high frequency discharge over the arc gap, and the choke-condenser unit to prevent the feed back of high frequency to the mains. Pfeilsticker claims that the electrical ignition of the arc suppresses air lines and gives a high light intensity. The sensitivity is generally greater than the ordinary mechanically interrupted arc, he states, except for P. The same general set-up, with modified circuit constants, has been used by Hemmendinger (1942) for the analysis of alloys, and Landergren (1945) who determined boron in silicate rocks and sediments. The latter is of direct application to soil work. The circuit is that of Pfeilsticker, except as regards the position of the rotating switch which operates on both current supplies through relays (Landergren, 1943). The powdered rock sample is mixed with an equal weight of B-free felspar and packed into a hemispherical cavity in 3 mm. Cu rod, this electrode being the cathode. The line B 2497.72A is used and compared with Sb 2598.08 or 2478.31A, Sb_2O being added to the extent of 2.5% in the final mixture as internal standard. The total exposure time is 2 minutes, comprising 240 discharges of an eighth of a second, so that the effective time is 30 seconds, with a current of 4 amp. Exposure is made through a step filter and the method of evaluation follows that of Kaiser (1941). The probably error for contents between 0.0025 and 0.03% B is given as $\pm$10%. B is visible down to 0.001%. Moritz and Schneiderhohn 1936) have described applications of the original interrupted arc to the determination of Sn in ores, whilst Schleicher and Kaiser (1936) used it in the qualitative analysis of electrolysed material concentrated from mine waters. It has also been used by Russian workers (Sventitski, 1937).

b. The Low Voltage Alternating Current Arc

Owing to the difficulty of maintaining an alternating current arc at low voltages, it has become the practice to run it with a superimposed high frequency Tesla spark similar to that used by Pfeilsticker. Pfeilsticker (1937) appears to be one of the few workers who have used a mechanically interrupted a.c. arc. Kingsbury and McClelland (1945) have employed, for zinc alloys, an a.c. arc activated by means of such a circuit, describing it as an intermittent alternating current arc, although no mechanical interrupters are included and the arc frequency is therefore that of the supply mains. When the high frequency circuit is properly adjusted, the high frequency discharge occurs only at or near the voltage peak of the alternating current wave. Kingsbury and McClelland (1945) employed a very large condenser of 48 mfd. in the arc circuit (C_3 in Fig. 23) so that each discharge was of constant energy corresponding to the amount stored by this condenser. McClelland (1946) has described the application of the method to (a) the determination of one or two elements present in small amounts in the residue or ash of a material, the matrix of which has been largely removed, and (b) the determination of a large number of trace constituents (at contents of 0.02-2.0%) in a variety of inorganic salts and precipitates. In the former method, which was used for Pb, Sn and Cr, a solution containing the extracted elements, a spectrographic buffer ($NaNO_3$) and the internal standard is prepared in as small a volume as possible, and one drop placed in the crater of each of two graphite electrodes. Both upper and lower electrodes thus carry the sample. One minute exposure is given with Ilford Special Rapid plates on a Hilger Medium Quartz spectrograph. The electrode separation is 4 mm., the current 4 amp. with the arc gap shorted (from Kingsbury and McClelland), and the arc imaged at the collimator. For the second method, using a large quartz instrument with Iso-zenith plates, in the 2500-3500A region, Fe was employed as internal standard for the following line pairs :

Mg	2802.7	—	Fe	2804.5	Mg < 0.2%
Mg	2779.9	—	Fe	2804.5	Mg > 0.1%, masked by Sn
Mn	2798.3	—	Fe	2804.5	
Pb	2833.1	—	Fe	2845.6	
Sn	2840.0	—	Fe	2845.6	
Cr	2849.8	—	Fe	2845.6	
Al	3082.2	—	Fe	3091.6	Masked by V
V	3110.7	—	Fe	3091.6	V > 0.25%
V	3185.4	—	Fe	3091.6	V < 0.5%
Mo	3158.2	—	Fe	3091.6	
Cd	3261.1	—	Fe	3254.4	
Cu	3274.0	—	Fe	3286.8	Very sensitive : low Cu only
Zn	3345.0	—	Fe	3450.3	Mo 3344.75
Co	3405.1	—	Fe	3450.3	
Ni	3461.7	—	Fe	3450.3	
Sr	3464.5	—	Fe	3450.3	

Ba, Ca, W, Ag, Ti and Si were not satisfactorily determined for diverse reasons. For the other elements, using a technique similar in general to that described above, an accuracy of ±5-10% was obtained. The pre-treatment necessary was to evaporate 0.02 g. of substance to dryness with HNO_3, dissolve in 0.5 ml. of a 10% solution of $NaNO_3$ in 2N.HNO_3, then re-evaporate and re-dissolve the residue in 1 ml. of a solution containing 1 g. of pure Fe per 100 ml. of 2N.HNO_3. This extract is added to the electrodes as described above. The technique should be applicable to many problems encountered in agricultural and biological work.

This type of a.c. arc with a high frequency activating current is described by Sventitski (1938, 1941) and Belkevitsch, Bruk and Sventitski (1941). Pfeilsticker (1940) has described the use of an a.c. arc (electrically controlled, without mechanical interrupter), with a high capacity condenser over the arc gap (500-2000 mfd.) and a high frequency activator with a low inductance and low resistance secondary in the Tesla transformer, for the quantitative determination of non-metals at low pressures (5-40 mm. Hg). This electrical set-up gives a low voltage spark-type discharge with instantaneous currents of several hundred amperes over the arc gap. This is adequate to excite the sensitive lines of the non-metals, for most of which down to 5-20 μg. can be detected in 2 mg. of material.

Braudo and Clayton (1947) describe a low voltage a.c. controlled arc, with a synchronizing and triggering current, that they employed for the analysis of Al and Al alloys.

Callon and Burgener (1944) have used for the analysis of aluminium ores a method of possible application to soils, in which the finely powdered material is allowed to flow down through the arc gap of a horizontal 220 volt a.c. arc.

Kaiser and Sohm (1941) have compared the Gerlach mechanically interrupted d.c. arc with the Pfeilsticker electrically ignited d.c. and a.c. interrupted arcs, the interrupter in the latter being in the high frequency side. When the number of interruptions, "rhythm" and effective current were the same, they found that essentially similar spectra were obtained.

c. "Universal" or Multisource Units

It is possible, by means of variation of the values of the resistance, capacity and induction in the various units in circuits of the Pfeilsticker type, to produce discharge conditions which can be varied at will from arc-like to spark-like. Sventitski (1942) pointed out that a spark-like discharge could be obtained by suitably choosing parameters of the high frequency oscillator and shunting the alternating current arc circuit with a condenser. In order to change from arc to spark conditions it is necessary, he points out, to decrease the duration of the arc flashes and to shunt the inter-electrode gap by a condenser. A device to interrupt the alternating current supply, thereby giving an arc suitable for easily melted alloys, is included, making it a true interrupted or intermittent a.c. arc. This type

of source has been employed in the analysis of non-conducting powders by Borovick (1943).

Hasler and Dietert (1943) have described a multisource unit, available in U.S.A. from A.R.L., whereby a similar variation from arc to spark conditions can be obtained by variation of the circuit conditions. In this instance both high and low voltage supplies are fed directly to the analytical gap, the Tesla transformer being omitted. Both supplies are half wave rectified direct current with a synchronous gap in the high voltage side. The conditions at the gap are shown on a cathode ray oscillograph. The use of this source is discussed by Hasler and Kemp (1944). Burdett and Jones (1947) have determined Fe, Na, V, Ni, Cr and Cu in cracking catalysts consisting mainly of Si and Al, using the multisource unit to excite the spectra. The sample was mixed with NH_4Cl and filled into a graphite centrepost electrode.

Walsh (1946) has described a unit similar in principle to that of Hasler and Dietert, but the details are quite different, particularly as regards the methods of triggering and the electrical constants of the discharge circuits. Either half or full wave direct current can be supplied to the arc gap, whilst alternate charging and discharging of the condenser is carried out by tuning the primary of the triggering circuit instead of by a synchronous spark gap. To ensure reproducibility, both the control gap and the analytical gap are illuminated with ultra-violet light from a mercury vapour lamp. Reports on the operation of the Walsh source so far cover only metals and alloys.

Braudo and Clayton (1946), for a high voltage high power and low voltage controlled a.c. arc, describe the use of a Trigatron auxiliary spark gap. This is a 3 electrode gap enclosed in a high pressure argon-oxygen mixture, which does not require irradiation with ultra-violet light. Caldecourt and Saunderson (1946) have developed an electronically controlled combined arc-spark source with the arc interrupted periodically, this being an advantage for samples such as Mg alloys. The arc current, when running, was supplied in pulses either directly from the a.c. mains or from a large condenser.

d. The High Voltage Alternating Current Arc

Duffendack and Thomson (1936) introduced a high voltage alternating current arc which has been widely used for certain forms of quantitative spectrographic analysis. A 2000-5000 volt a.c. supply at 50 cycles is connected through a large ballast resistance over a short gap of 1-3 mm. The current is of the order of 2-5 amp. and the arc has the advantage that the high initial voltage over the short arc gap is sufficient to break down the air resistance, thus making it self-igniting. The voltage over the arc after it is made, for the remainder of the half cycle, is of the same magnitude as that in normal d.c. or a.c. arcs, that is, between 40 and 100 volts, and the source is essentially a spark-ignited arc. It is claimed that the making and breaking of the arc twice per cycle eliminates difficulties ascribed to the

wandering of the cathode spot in the direct current arc. The usual technique when dealing with biological samples is to obtain an extract of the material in solution and to dry a drop of the liquid to be examined on each electrode. The method is much more suitable for the analysis of solutions than of non-conducting powders, as Melvin and O'Connor (1940) have pointed out in their work on the analysis of fertilizer powders, and most of the applications have dealt with solutions. Oshry, Ballard and Schrenk (1941) used a 2200 volt supply a.c. arc over a 1 mm. gap at 3 amp. for the determination of Pb, Cd and Zn extracted from dusts, fumes and ores, placing one drop of nitric acid solution of the material on the tip of each copper electrode. The concentration ranges covered were Pb 0.02-5.0 mg. per 50 ml., Cd 0.025-15 mg. per 50 ml., and Zn 0.25-50 mg. per 50 ml. Bi was the internal standard used. On the other hand, for the determination of the major constituents of mineral powders, the same workers (Oshry, Ballard and Schrenk, 1942) have employed a high voltage 2200 volt d.c. arc with currents up to 5 amp., filling the solid material mixed with NiO and graphite powder (12 mg. sample, 1 g. NiO, 0.5 g. graphite) into graphite electrodes 3.2 mm. in diameter with a boring 1.5 mm. deep and 1.3 mm. diameter. An accuracy of $\pm 5\%$ for contents of Si, Fe and Al up to 100% was obtained. The lower electrode was the anode, the electrode separation 1.25 mm. and a stream of air over the arc prevented condensation in the upper electrode. Si 2516.1A, Fe 2522.9A and Al 3082.2A were all measured against Ni 2540.0A.

Details of technique with the high voltage a.c. arc applicable to extracts of soils and plant materials are to be found in numerous papers. Duffendack and Wolfe (1938 a, b) report the following ranges of concentrations as suitable for application to the electrodes: Al_2O_3 0.0001-0.014% ; CaO 0.000054-0.005% ; MgO 0.00006-0.0036% ; SiO_2 0.001-0.1% ; Cr 0.000075-0.01% ; Cu 0.000016-0.005% ; Fe 0.00001-0.01% ; Mn 0.00001-0.00052% ; Ni 0.000075-0.01% and Pb 0.00002-0.0034%. Owens (1938 a) mentions that the advantages of the a.c. arc include ease of maintenance, ease of control of excitation conditions, high sensitivity, low background density, and accuracy, stating that in general the sensitivity of detection of any metallic constituent of a chemical material is around 0.0001%, claiming that for many elements, such as P, V and Ag (in NaCl solution), the sensitivity is 5 to 10 times as great as in the d.c. arc. Ruehle and Jaycox (1940) report the determination of Ba, Sr, Te and P in dilute solutions. They point out that the high voltage a.c. arc method is considerably more dangerous to the operator than spark or d.c. arc methods, and that safety precautions must be rigidly maintained. Access to the arc stand must be possible only when the supply is completely disconnected. Wilson (1944) has used ammonium molybdate as internal standard substance for the determination of B, Si, Fe, Mn, Al, Cu, Na and Co in magnesium chloride solutions. Parks (1942) has determined B in synthetic soil mixtures by filling the dry powder into a cavity in the lower carbon electrode of a high voltage a.c. arc. B 2497.7A was compared with internal standard Sn

2429.5A. Interference was caused by NaOH, $AlCl_3$ and, to a lesser degree, Na_2SO_3, $CaCl_2$, NaCl and NH_4Cl in 10% amounts. A 50 mg. sample was mixed with 100 mg. of $CaCO_3$ and 1 ml. of 0.03% $SnCl_2$ solution added. The precision was of the order of 3-10% for a single determination.

Wolfe and Fowler (1945) used polystyrene coated graphite electrodes on which 0.15 ml. of solution was dried. Percentages detected in a 10% $FeCl_3$ solution with a 2200 volt a.c. current arc, 5 amp., 1.5 mm. separation, were: Al 0.0001%, Sb 0.02%, As 0.01%, Bi 0.005%, Cd 0.0001%, Cr 0.005%, Co 0.001%, Cu 0.00005%, Mg 0.0001%, Mn 0.0001%, Mo 0.002%, Ni 0.001%, Ti 0.02%, V 0.03%, Zn 0.001%. Line pairs for most of these elements, using Ge as internal standard, are given, as is a concentration method for removal of Fe (see p. 126). Efendiev (1945) reports the use of the high voltage a.c. arc for the determination of Au, Ag, Cd, Hg, Mo, Co, etc., in ores and minerals after extraction and introduction of the extract into the electrode. Fast and Nielsen (1947) have investigated the effect of alkali and alkaline earth salts on the determination of Si in the high voltage a.c. arc.

Because of the very short arc gap generally employed, it is necessary to have an arc stand which can be precisely controlled, whilst its insulation must be of a considerably higher standard than generally employed in arc work. Reference has already been made to descriptions of suitable stands (p. 57). As there is little consumption of electrode material during a burn the arc position can be fixed prior to its commencement.

The high voltage alternating current arc method would appear to be of use in certain circumstances but is not of such wide general application as the ordinary direct current arc. A recent study of its characteristics is that of Boettner and Tufts (1947).

Chapter 8

SPARK METHODS OF SPECTROGRAPHIC ANALYSIS

The spark source utilizes the energy from an oscillating high voltage discharge, generally in air, between conducting electrodes. The applied voltage is generally between 10,000 and 50,000 volts. The nature of the discharge is determined by the resonance of the secondary circuit, which can be tuned by varying the capacity and inductance introduced into it. Quite different spectra are given by uncondensed and condensed sparks, the latter being much more intense, but containing many air lines (N_2 and O_2) which can be suppressed by the introduction of self-inductance into the secondary circuit. The high voltage supply generally comes from a single phase transformer of a rating up to 2 kw. Much work has been done with $\frac{1}{4}$ kw. sets, which is the size normally supplied in Britain.

In the spark there is an oscillatory discharge each half cycle, which is more prolonged with increased self-inductance. The auxiliary synchronous gap used by Feussner (1932) is so arranged that the number of oscillations per discharge is cut down. This can also be achieved by tuning the secondary of the transformer into phase with the mains frequency. The so-called direct current spark used by a few workers is a half wave rectified spark.

A high frequency or Tesla spark discharge is produced by coupling the main secondary circuit, containing an auxiliary spark gap, to the circuit containing the analytical gap by means of a high frequency transformer. Gerlach and Schweitzer (1930 a) and Gerlach and Gerlach (1933) have used this set-up for the analysis of filter residues, etc., obtaining a spectrogram which was generally of an arc-like character, and Sibaiya and Rao (1941) used it for the analysis of fruits. The Tesla circuit is of interest in view of its use as an activator in arc work (Chapter 7).

Most spark circuits are of interest chiefly for the analysis of metals and alloys, where the sample can form the electrode itself, and even here the presence of inhomogeneities in the metal may lead to difficulties. In view of its limited applications to biological work, the discussion of the general principles of the spark source has been intentionally curtailed. It is described in more detail in most of the standard textbooks. The spark source is generally not so sensitive as the arc, and finds its application chiefly for the analysis of constituents which are present in above trace quantity. Where conditions are favourable, its reproducibility may exceed that of the arc.

Direct applications of the spark method to the type of material encountered in biological work have been restricted, because of the selective nature of the spark discharge. Foster, Langstroth and McRae (1938) have determined Na and K in glandular secretions by first evaporating a buffer solution containing an internal standard and then an aliquot of the unknown solution on a copper-plate electrode and sparking to a pointed copper electrode. Pb and Cd were the internal standards for K and Na respectively, whilst the buffer salt was lithium tartrate. The probable error is given as approximately $\pm 4\%$. Using similar electrodes of Cu, Ag or Al in conjunction with a rectified high voltage source the same authors had previously reported the determination of Pb in biological fluids (Foster, Langstroth and McRae, 1935) whilst Foster and Horton (1937) determined B in plant materials in the d.c. spark. An interesting photometric process involving the addition of a known amount of B to the unknown sample was employed.

Using a spark unit with a high input power, success has been obtained in the analysis of powders similar in composition to soils by Churchill and Russell (1945). Aluminium ores have been analysed for Al, Si, Fe and other major constituents by making a soft pellet of the sample with 5 parts of NaF and 12 of powdered graphite and sparking in the pellet holder of a Petry spark stand. The lower electrode was of graphite, and the ARL-Dietert spark source was used at a power setting of 2 kw. Standard deviations of under $\pm 3\%$ are reported.

Several methods for the introduction of the sample into the spark gap in solution have been suggested. Lundegårdh (1929) suggested a method in which the solution was fed to the electrodes from a pipette, but found (Lundegårdh, 1934, 1936) that an electrode which dipped into a reservoir of the sample was more satisfactory. In the immersion spark apparatus the whole electrode assembly is mounted on a cam which submerges both electrodes in the solution being examined once per second, the spark being cut off during the period of immersion. Both electrodes are generally of carbon, but the lower electrode can consist of a liquid surface, in which case the upper electrode is Al, Cu or Au. Lundegårdh (1936) has discussed the sensitivity of the different elements in the condensed spark.

Twyman and Hitchin (1931) have described a solution spark equipment which they employed for the determination of the chlorides of Cu, Zn, Bi, Pb, Ni and Co in HCl solution in concentrations of 0.01-1.0%. The sparking tube has been modified by Twyman, Zehden and Dreblow (1940) who substitute a bored graphite electrode for the silica tube containing a gold electrode. Amongst others who have employed a solution spark method are Uzumasa and Okuno (1934, 1935) who give data for Ag, Al, Ba, Ca, Cr, Co, Fe, Mg, Mn, Ni, Sr and Zn.

Pavlovschi and Mavrodineanu (1941) have used electrodes of porous sintered quartz to which solutions are drawn automatically by capillary attraction, excitation being by Tesla high frequency spark. Rohner (1937)

absorbed the sample on gelatine gel and analysed with high frequency spark. Jolibois, in a series of papers (e.g. Jolibois, 1936; Jolibois and Bossuet, 1937, 1939) has studied the discharge between a Pt electrode and a liquid surface, and gives in the last paper limiting concentrations for the detection of 21 metals.

Duffendack, Wiley and Owens (1935) and Duffendack and Thomson (1936) have described methods whereby solution is fed to jets at the electrodes, using a 1 kw. 25,000 volt source, without capacity or induction. The technique was applied to the determination of Na, K, Mg and Ca in urine with Cd as internal standard. Curves were obtained for the following concentration ranges: Na 0.1-1.2%, K 0.1-1.2%, Mg 0.0025-0.015%, Ca 0.04-0.15% and interference effects are discussed.

The method of Sloviter and Sitkin (1944) involves the use of one drop of solution on an absorbent graphite electrode specially prepared by heating for one hour at 900-1000°F. The source is an uncontrolled condensed spark with only sufficient inductance to suppress air lines. Suitable lines for Mn, Cr, Ni, V, Mo and Cu are given, together with Fe comparison lines. Details given apply to the determination of these elements in steel.

Bertrand (1942) has used the fused salt technique of Gramont (1922 a, b) for the determination of V in plant materials by means of the spark. The sample is fused in a small platinum spoon containing molten alkali carbonate which forms the lower electrode.

The spark has also been employed in conjunction with other sources, particularly the flame, in order to obtain greater sensitivity than given by the latter alone. Methods in which the emission of a flame charged with spray has been increased by the use of a spark discharge through the flame have been described by Hultgren (1932) and Lundegårdh and Philipson (1938). The analysis of the alkali and alkaline earth metals is little affected by the addition of the spark to the normal Lundegårdh flame, but a great improvement is obtained with Mg whilst Be, B, Al, As, Pd, Cd, Sn, Sb, Ba, Os, Pt, Au, Hg and Pb all show sensitivities of M/1000 or better. A suitable spark unit has an input of up to 4 amp. in the primary circuit whilst the secondary circuit includes a capacity of 17,000 cm. and self-inductance of 0.2-0.8 mh. A secondary voltage of 15,000 volts is suitable: the discharge should be intermittent with periods of about a quarter second duration to prevent heating of the copper electrodes. Results obtained by the Lundegårdh-Philipson technique are quoted by Norinder (1938, 1942) for the determination of Mg in blood.

For the determination of metalloids, Levintov (1945) has used a combined arc-spark source, in which a direct current arc is employed to volatilize the sample, whilst an intermittent spark discharge, synchronized with an opening in a disk at the spectrograph slit, provides the energy for main excitation of the material in the arc column.

Chapter 9

DIRECT PHOTOMETRY

When a permanent record of a spectrogram is not required, and in particular when one element alone is to be determined, the direct measurement of the intensity of the spectral lines concerned by a photoelectric cell or some similar means has much to recommend it, and the possibilities have been investigated by numerous workers. The method was reported by Lundegårdh (1930, 1934) who employed a double monochromator to obtain good dispersion and amplified the photo current given by a sodium cell by means of a valve amplifier to obtain a suitable galvanometer deflexion. Amongst elements with lines suitable for analysis Lundegårdh mentions Ca, Na, Sr, Tl, Cu and Ag. The weakness of the method lay in the instability of the amplifier, and this led Jansen, Heyes and Richter (1935) to employ a Lindemann electrometer as measuring instrument for the determination of K, Na, Li, Rb and Cs in an air-acetylene flame, using a caesium photo-cell. The use of this method necessitated a constant source such as is provided by a flame, as periods of 10 to 50 seconds are recommended for the electrometer reading. Three to five readings were taken for each determination and the reciprocal of the mean time was found, within certain concentration limits, to be in linear relationship with the concentration. Errors were generally within $\pm 5\%$. With a Hilger monochromator the following wavelengths and concentrations were suitable :

Li	6710A	1/5000 — 1/500 M
Na	5890A	1/20,000 — 1/800 M
K	7660A	1/20,000 — 1/800 M
Rb	7800A	1/10,000 — 1/800 M
Cs	8520 or 8940A	1/5000 — 1/500 M

Thanheiser and Heyes (1939) have described the use of two monochromators and electrometers, requiring two operators, for the determination of Cu, Mg, Mn in Al in the spark, an Al line being employed as internal standard.

The use of the Beckman spectrophotometer for the measurement of line intensities in the Lundegårdh flame has been described by Müller (1947).

These methods used a monochromator to isolate the required wavelength, but a closely allied method is that employing a spectral filter to cut off all radiation except that of the required wavelength. The energy available is then much greater and the governing factor is the efficiency of the filter in stopping unwanted radiation. Jansen, Heyes and Richter (1935)

attempted to determine Na and K using filters instead of a monochromator, but failed to get reliable results when the concentration of extraneous elements approached that of the element being determined.

The filter method has been used extensively, especially in Germany, for the rapid determination of K in solution, employing the K lines in the red. The application has generally been to the determination of K in Neubauer seedlings in connexion with the assessment of soil fertility. The method was used on a routine scale by many workers, being described by Schuhknecht (1937), Goy (1937), Schmitt and Breitwieser (1938), Giesecke and Rathje (1938), Kertscher (1938), Lehmann (1938), Schnell (1941), Rauterburg and Knippenburg (1941), Arnd and Leisen (1942), Herrmann and Lederle (1942), Herrmann (1943) and Riehm (1942, 1945). Schmitt and Breitwieser compared the Siemens and Zeiss equipments, finding both suitable for the determination of K in Neubauer seedling ash extracts. The Schuhknecht method, with a filter of BG 3, RG 19 and RG 8 Schott glasses, was used by Lundegårdh and Boratynski (1938). They worked with concentrations of 0.00025-0.004 M. K and concluded that for many purposes, e.g., analyses of plant ash and soil extracts, it is of service if an accuracy of no more than $\pm 10\%$ is adequate. Ca can cause difficulties in the analysis of soil extracts. NH_4Cl introduces errors by depressing the temperature of the Lundegårdh flame source.

Barnes, Richardson, Berry and Hood (1945) have described a compact flame photometer in which the solution is sprayed into a Fischer type burner using coal gas. Suitable Corning glass filters for Na, K, Ca and Li are detailed, and it is stated that analyses for Na and K to an average accuracy of $\pm 3\%$ are quickly carried out. This depends on a single galvanometer deflexion for the element in question, but Berry, Chappell and Barnes (1946) have described a modification with a dual optical system in which the internal standard principle can be introduced. In this paper the effects of various extraneous substances on the determination of Na and K by both methods are compared, and the improvement effected by the use of Li as an internal standard pointed out. Boon (1945) has discussed the relative values of different types of filters, photocells and sources in flame photometry. The determination of the alkali metals in the flame, in the presence of Ca and Mg, is considered, and the determination of K and Na in flour taken as an example.

A method using as assessment the point of visual disappearance of the spectral lines when viewed through a wedge-shaped filter of a coloured solution ($CuSO_4$ or $KMnO_4$) is described by Rusanov (1934 b), the normal Lundegårdh atomizer and flame being used for solutions of Li, Na, K, Ca, Sr, Ba and Tl. The application of the method to the determination of the alkalis and alkaline earths in Al and Pb metals is described by Rusanov and Bodunkov (1936). Rusanov and Kunina (1937) describe the determination of In. For determinations of B in plant materials McHargue and Calfee (1932) and Calfee and McHargue (1937) have used the extinction of the

methyl borate bands in a flame when observed through a $KMnO_4$ solution. Weber and Jacobson (1938) simply observed the duration of the green colouration.

In the past few years, developments in electronics, stimulated by war conditions, have led to the production of electron photo-multiplier tubes which are suitable for use in the direct measurement of the intensity of spectral lines. The photo-multiplier tube is a high vacuum photo-tube in which the photocurrent produced by the incidence of radiation on the light sensitive cathode is multiplied by secondary emission occurring at successive electrodes within the tube. These electrodes are generally charged with incremental voltages in about 100 volt steps, a total of some 1000 volts being over the tube. In the direct methods now being developed, monochromatic radiation of a single spectral line is isolated in the spectrograph and passed, either directly or by means of a narrow mirror, into the narrow entrance slit of a photo-multiplier tube. The photocurrent produced by spectral lines of the intensities normally used in spectrographic analysis can be measured directly by sensitive milliammeters or similar measuring devices. Previous to the introduction of the photo-multiplier tube Duffendack and Morris (1942) described the use of a Geiger-Muller counter.

A single photo-multiplier tube was used by Rank, Pfister and Coleman (1942) and Rank, Pfister and Grimm (1943) in their work on Raman spectra, but the advantage of the internal standard method soon led to the use of this method by Boettner and Brewington (1944) for the analysis of Ca in NaOH with Sr as internal standard in the high voltage a.c. arc, of Al in NaOH in the d.c. carbon arc, and of Al in Mg alloy in the spark. They employed RCA931 tubes set to the required positions in the focal plane of a grating spectrograph. Hasler and Dietert (1944) built an instrument with twelve tubes mounted in the spectrograph, so that twelve lines could be measured simultaneously in the 2000-6000A region. Because of space difficulties, mirrors were used to reflect the spectral lines into the entrance slits, which were wider than the lines being measured. With this instrument lines as close together as 2.2A could be measured. The current from the photo-tubes was amplified and recorded on receivers of an integrating type, giving integrated line intensities in terms of dial readings on counters. The exposure of a sample in a spark discharge is continued until a definite count is got for the internal standard, when the counters for the other elements give a measure of their respective contents, with, it is claimed, errors of the $\pm 3\%$ order. An instrument of this type is available commercially in the United States of America.

In order to avoid being limited to a number of pre-determined lines, Dieke and Crosswhite (1945) have used a moving slit to scan the spectrum in conjunction with an electronic recording microammeter, getting by this means a record of the whole spectrum similar to that given for a spectrogram by a recording microphotometer. This set-up is suitable only for a source of constant emission, such as a flame, spark or a.c. arc, compared with the

integrating recorder which can take care of variations in the relative intensities of different elements at different times.

Nahstoll and Bryan (1945) have measured the ratio of the outputs of two photo-multiplier tubes by means of a vacuum tube voltmeter, in the determination of Al in Mg alloys, with maximum deviations of $\pm 2.5\%$ and average deviations of $\pm 1.3\%$ over an 8 hour period, slightly larger over 14 days. The multiplier tube used gave an amplification of 200,000 times. Saunderson, Caldecourt and Peterson (1945) integrated the photocurrents by storage in condensers and used direct current amplifiers to measure the stored charges. Essentially the method involves allowing the condensers to discharge slowly through a resistance and using the amplified current to operate a relay when the voltage falls to a predetermined value. A strip of recording paper then measures the time required for the condenser voltage to fall to this value. The integration of variable light intensities by charging a condenser with the photocurrent has also been carried out in Russia by Sedov (1943) and Hopstein, Pedos, Prokofiev and Sventitski (1944). Saunderson, Caldecourt and Peterson (1945) introduced a means of automatic background correction in which the condenser is charged for a period by means of the line+background intensity and then discharged for a similar period by the background intensity adjoining the line. By means of prisms, lines 2A apart could be dealt with. Standard deviations for Al, Ca and Zn in alloys were less than 2.5% whilst data for Mn, Si, Cu and Be also showed good precision. Kessler and Wolfe (1947) have also described the measurement of intensity ratios by means of multiplier phototubes.

The use of the cathode ray oscillograph as the indicating device in conjunction with multiplier photo-tubes has been described by Dieke, Loh and Crosswhite (1946), Dieke and Crosswhite (1946) and Craggs and Hopwood (1946). Dieke (1945) has discussed the properties of various types of photo-multiplier tubes, whilst Carpenter (1946) has applied this type of tube to the design of a microphotometer.

Up to now there have been no reports of the use of electron photomultiplier tube direct photometric determinations applied to analysis of soils or plant materials, but there is no doubt that this method could be very usefully combined with the Lundegårdh flame source for the routine determination of the alkalis and alkaline earths. Its application to the determination of trace constituents at low concentrations in the arc would probably be more difficult, but not impossible if one of the integrating methods were employed. It would appear, however, that the maintenance of the equipment is liable to be troublesome, in its present state of development, unless workers skilled in the upkeep of electronic equipment are available.

Chapter 10

NOTES ON THE DETERMINATION OF INDIVIDUAL ELEMENTS

There are certain points in the determination of various elements which it has not been convenient to mention in the foregoing chapters. It has therefore seemed desirable to include a few notes on these elements, the treatment of which is not intended to be exhaustive, but merely to indicate the lines of approach. Limitations of space have necessitated the discussion only of elements in which points of particular interest arise.

Alkali Metals

When present in adequate quantity, the most satisfactory determinations of the alkali metals are those by flame methods, discussed in Chapter 4.

In the d.c arc, Helz (1945) has given details of a method for the determination of K, Na and Li in cement. For Na and K, the sample is mixed with three times its weight of a mixture of 60% SiO_2, 14% Al_2O_3, 20% $CaCO_3$ and 6% Li_2CO_3. After fusion and grinding, 10% Ag_2O is added. 30 mg. of the final product are arced at 10 amp. as the anode of a 4 mm. d.c. arc in a composite graphite electrode of the type described by Scribner and Corliss (1943). Na 8194.8A and K 7699.0A are measured against Ag 8273.5A and Ag 7687.8A respectively. A range of 0.05 to 1.5% Na or K is covered. For Li, the sample is mixed with a powder containing 70% graphite and 30% $SrCO_3$ and Li 3262.6A measured against Sr 3301.7 or 3322.2A, covering Li contents above 0.05%. A ground glass screen near the arc was employed to reduce intensities. Whitehead and Williams (1945) describe the d.c. arc determination of Na and K in HCl solution with Co and Sr respectively as internal standard. Urbain and Wada (1936) recommend determination of alkali metals in a ZnO base with copper electrodes in the d.c. arc with Cd as internal standard.

Strock (1936 a, b) has studied the determination of Li in rocks, with Sr as internal standard, in the cathode layer arc, and shown that there is an enhancement in the presence of NaCl. Accurate results for all the alkali metals in an arc source probably depend on the availability of a suitable internal standard, and, if feasible, one of the alkali metal group itself is the most likely to give reliable results. Generally, however, it will be found that materials being examined contain all five alkali metals, so that a less satisfactory standard must be chosen.

Erämetsä, Sahama and Kanula (1941) have developed the work of Goldschmidt, Bauer and Witte (1934) on the determination in rocks and minerals of Rb and Cs in the cathode layer arc, introducing photometric methods of measurement.

Amongst those determining alkali metals in the spark, Foster, Langstroth and McRae (1938), who determined Na and K in glandular secretions, may be mentioned, whilst Oplinger (1947) has used a 2200 volts a.c. arc at 2 amp. for the determination of Li, Na and Fe in lithium-bearing ores.

Boron

The spectrographic detection of B is made either from the sensitive B doublet at 2496.78/2497.73A or by means of the bands in the green obtained when methyl borate is introduced into a flame.

The B lines mentioned are very sensitive and can be observed in a silicate base in a 4 amp. d.c. arc between copper electrodes down to 1 p.p.m., with the material in a cathode with a cavity 2 mm. deep, 2 mm. diameter and 3 mm. outside diameter. The anode should be of 8 mm. copper rod, as melting occurs with lighter electrodes. An arc 4 to 5 mm. long, with the light from the whole arc column being employed, is most suitable. Sixty seconds exposure is generally adequate to volatilize all B from the sample. The use of copper or some other metallic electrode is often necessary because all but the most expensive carbon electrodes contain B as an impurity in very appreciable quantity. This is unfortunate because of the difficulty of obtaining reproducible results with non-conducting powders in metallic electrodes in the d.c. arc. This is accentuated by the lack of a suitable internal standard for B at a wavelength near 2500A. Elements such as Sn, Au or Be have not proved too satisfactory in the d.c. arc. Be is probably most promising, but the lines near 2500A are not quite sensitive enough, and Sn has been very commonly used.

Goldschmidt and Peters (1932 c, d) report the semi-quantitative determination of B in rocks and soils. They found the same B sensitivity in standard mixtures prepared from H_3BO_3 and from B combined in tourmaline, but in practice it is probably best to employ one of the less volatile sources of B. Finely ground Pyrex glass, of known B content, is a convenient material.

When employing copper electrodes for B, care must be taken to avoid Cu contamination of the laboratory atmosphere for subsequent determinations of Cu on carbon electrodes. Because of this and because of the noxious nitric fumes produced by a copper arc in air, adequate ventilation over the arc is essential.

Parks (1942) employed Sn 2429.5A as internal standard to B 2497.7A for synthetic soil mixtures analysed in the high voltage a.c. arc.

The spark has been used by Foster and Horton (1937) and by Wilson (1942) and Wilson and Fieldes (1942 c) for the determination of B in plant materials. The latter fuse the ash in alkali carbonate, acidify with nitric

acid and add mannitol as a buffer before applying the solution dropwise to copper electrodes. Pears, apple leaves and pine needles were examined.

Landergren (1945), as already noted, has employed the interrupted d.c. arc, with Sb as internal standard, for the determination of B in rocks and sediments. Others who have discussed the determination of B in geological materials include Wasserstein (1943) for B in braunite and manganese ores, and Rafter (1945) for B in coal. Wright (1937) describes a method for B in soils.

Determinations of B by means of the green flame coloration are discussed by Stahl (1931 a, b) and applied to agricultural materials by McHargue (1933), McHargue and Calfee (1932), Calfee and McHargue (1937) and Weber and Jacobson (1938).

Cobalt

For the determination of Co in soils, plant materials and animal organs the greatest possible sensitivity is generally required. The practical importance lies in the occurrence of cobalt deficiency in sheep and cattle (Mitchell, 1945). There is little or no evidence of deficiency or excess problems arising in practice as far as plant growth is concerned.

Co is best determined in the d.c arc, where the 3453.5A line can be observed, using the cathode layer technique, down to about 2 p.p.m., corresponding to 0.006 μg. in the electrode. This Co line lies rather close to the Ni line at 3452.9A, so that a large spectrograph is essential, especially as it is desirable to use the 3451.9A Fe line of the doublet 3451.9/3452.3A as internal standard. This iron line is satisfactory at concentrations between 2 and 40% Fe_2O_3, and Scott (1946) has shown that this cobalt : iron pair is practically unaffected by the composition of the matrix. The quantitative determination of cobalt using the line 3453.5A can be made over the range 10-3000 p.p.m. with errors of single determinations not exceeding 10%. In fact over the best range, about 70 to 700 p.p.m., errors seldom exceed half of this.

The only element likely to interfere by coincidence with determinations of Co with the 3453.5A line is Cr which has weak lines at 3453.3 and 3453.7A, but for Cr contents below 3000 p.p.m. no interference is found.

Other possible Co lines include Co 3405.1A, with a sensitivity of about one fifth of that at 3453.5A, and the line at 2407.3 which is almost as sensitive as the latter, although lying in a series of SiO bands. P. H. Lundegårdh (1946 a) reports the use of Co 3449.2A.

For the determination of cobalt in solution the 8-hydroxyquinoline concentration method into an Al_2O_3 base can be employed, as described in Chapter 11.

Ambler and Griggs (1941) have determined cobalt in pectinates by the Lundegårdh method, using the Co 3526.8A line, with a concentration of 0.00025-0.002 M in the solution. The amount necessary on a Ramage spill to produce a suitable spectrogram is 0.0025 mg.

Fluorine

Spectrographic determination of F has been reported in phosphatic rocks, glasses, waters, teeth, bones, protective layers on metals and in gases. It is the only element whose direct determination depends on a band rather than a line, and one of the few elements which can conveniently be determined indirectly (by the formation of SiF_4 and the determination of Si).

The strong CaF bands appear in arc, spark and flame sources when fluorides and Ca salts are present, as a sequence of double headed bands degraded to the red. The $0,0R_2$ and R_1 heads are at 5291.0 and 5292.9A. A weaker series has $1,0R_2$ and R_1 heads at 5145.4 and 5146.4A. Similar series of bands are obtained from SrF and BaF, so it is possible that there may be interference effects of Sr and Ba on the CaF intensities.

Ryde and Yates (1926) reported the determination of F in opal glasses in one of the earliest recorded uses of the CaF band for analytical purposes. Papish, Hoag and Snee (1930) observed the band with $KF+CaCO_3$, $Ca(NO_3)_2$, $CaCl_2$, $CaSO_4$, and $Ca_3(PO_4)_2$ in an 8-10 amp. d.c. arc with the sample in the graphite anode, the voltage drop being 60 volts, and also in high frequency and condensed sparks. 10 mg. ashed samples of teeth and bones were arced directly, but a concentration method for samples with low contents is also reported. 5g. of bone ash is treated with 15 ml. of 25% H_2SO_4, and distilled into lime water. The distillate is dried and spectrographed. The lowest quantity detected on the electrode was 0.009 mg.

With 12.5 mg. samples in the graphite anode of a 15 amp. d.c. arc, Petrey (1934) found a useful working range of 0.05-1.5% F in a $CaCO_3$ base and reported analyses of waters, as did Churchill (1931 a, b) and Braidech and Emery (1935).

Further work on bones and teeth is given by Boissevain and Drea (1933) and Glock, Lowater and Murray (1941) whilst Balz (1938) reported the detection of F as CaF_2 in the protective layer of electron alloy.

Ahrens (1942) analysed phosphatic rocks by a method which should be applicable to phosphatic fertilizers. The source employed was a 6.5 amp. d.c. arc running off 250 volt mains, with a carbon anode 10 mm. diameter with a cup to hold 50 mg. of material, which consisted of the sample mixed 1 : 1 with a 75% charcoal : 25% $CaCO_3$ mixture. This burnt to completion in about 50 seconds, and 3 such exposures for each sample were superimposed. Quantitative estimation was by means of a logarithmic sector and measurement of the height of the CaF 5291A band. Standards on each plate covered the range F 0.01-3.0%. Silica was found to interfere above 65%, giving low results. The accuracy obtained was $\pm 12\%$ for 0.025-3.0% F. SrF and BaF bands were also investigated (Ahrens, 1943 b).

McNally, Harrison and Rowe (1947) report the detection of 1 p.p.m. F in a 100 mg. sample in a hollow cathode discharge source, using the F line at 6856.02A, when normal plates are employed, and a greater sensitivity with hypersensitized plates.

The indirect method for F was reported by Paul (1936, 1938) and by Paul and Kareth (1940). Paul and Kareth treated both organic and inorganic substances with H_2SO_4 and anhydrous $CuSO_4$, in the presence of SiO_2, at not less than 135°C., and absorbed the SiF_4 in molten 1 : 9 PbO+ B_2O_3 at 530°C. The cooled mass was employed as the core of a carbon electrode and the Si content obtained from Si 2881.6A : Pb 2873A intensity ratio for contents down to 0.005% Si, with an error of 15-20%.

Roche (1930) has discussed the determination of F as SiF_4 or BF_3 in the gaseous state.

Lead

The accurate determination of traces of Pb has proved rather troublesome in the d.c. arc, because of the rather greater volatility of Pb than of most other constituents which are normally determined. Elements such as Sn, Bi, Cd and Zn behave in a similar fashion, and one or other of these has generally been selected as internal standard for Pb. Sn would probably be the most suitable, but it is seldom that Pb has to be determined in a series of materials all of which are free from Sn, hence the more general adoption of Bi. The 2833.1A Pb line is used by practically all workers.

Cholak and his collaborators (Cholak, 1935 a, b ; Cholak, Hubbard, McNary and Story, 1937) originally placed the sample in the cathode but later (Cholak and Story, 1938) changed over to the anode. Solutions containing 0.01-0.2 mg. Pb and 1 mg. Bi in 100 ml. were applied to a cratered graphite electrode and arced at 10 amp. for 3 minutes with a 5 mm. separation from a pointed graphite counter electrode. Duffendack, Thomson, Lee and Koppius (1938) report an arc method determining down to 0.1 mg. Pb per litre with as little as 2 drops of sample. Jeppesen, Eastmond and Logan (1944) determined Pb in the ash (500°C.) of pectinous materials by mixing with 4 parts of a base containing silica, lithium, sodium, calcium and magnesium carbonates, alumina and ferric sulphate, with bismuth as internal standard. 15 mg. of material are arced for 30 seconds at 15 amp. in a graphite anode electrode with a central graphite post. The ultimate sensitivity is 2×10^{-4} mg. Pb in the electrode. This method is applicable down to 1 p.p.m. Pb in the original material or 500 p.p.m. in the ash. Using the cathode layer arc, the practical lower limit of 500 p.p.m. in the material filled into the electrode has also been obtained, because of the presence of around 5% Fe_2O_3 in the samples. In the absence of Fe a lower limit of determination should be possible. By the semi-quantitative cathode layer arc technique Pb is detectable at 10 p.p.m. With the 8-hydroxyquinoline, tannic acid, thionalide concentration process (see p. 123), contents below 1 p.p.m. in the original can be determined. Numerous workers have determined Pb after concentration, principally with H_2S (Chapter 11).

Schroeder and Lythgoe (1941) have determined the Pb content of ciders and vinegars in the d.c. arc, with calcium acetate as buffer and Bi as internal standard. Kent (1942) determined Pb, Sn and Ag in flour, wheat and bran,

with the ash in copper electrodes, using only 2 amp., again with Bi as internal standard.

A discharge of the high voltage a.c. arc type would appear to be favourable to the determination of Pb in solutions (Thomson, Sawyer and Duffendack, 1938 ; Sawyer, Waggoner and Erickson, 1940). The sensitivity is greater than that given by the normal d.c. arc, Duffendack and Wolfe (1938 a, b) reporting a sensitivity of 0.00002% with one drop of the solution applied to the electrodes. This improvement in the sensitivity in the high voltage a.c. arc would appear to be general with the more volatile trace constituents, occurring also with Sn, Zn, Bi and Cd. Sensitivities for Pb, Cd and Zn extracted from dusts, fumes and ores are given by Oshry, Ballard and Schrenk (1941).

Some advantages have also been claimed for the low voltage a.c. (Kingsbury and McClelland, 1945) and interrupted d.c. arcs (Scott and McMillen, 1938) for the determination of Pb and other volatile constituents, including some of the metalloids (Riedl, 1932). Spark sources have been used by Foster, Langstroth and McRae (1935), Cruse and Schubert (1936) and Gerlach and Gerlach (1931), the latter making use of the Tesla discharge.

Pb is moderately sensitive in the Lundegårdh flame and can be determined in the concentration range M/200—M/4000 by the 4057.8A Pb line. The relative insolubility of $PbCl_2$ must be kept in mind when working with solutions.

Phosphorus

A group of 4 lines between 2530 and 2560A can be used for the detection of P in an arc source when it is present in moderate amount. The strongest line 2535.65A coincides with a very strong Fe line at 2535.60A, so that in practice only the 2553.28A line is feasible, and this lies near weak Fe, Co and Ni lines. The P lines at 2534.01 and 2554.93A are not sensitive enough for general use. Some workers, e.g., Ewing, Wilson and Hibbard (1937), quote erroneous P wavelengths, which appear in the wavelength tables of Kayser (1926), where all 4 lines are given approximately 0.7A too high.

Ewing, Wilson and Hibbard (1937) and Hibbard (1941) determined P in HCl extracts of plant ash. Extract from 50 mg. of ash is made to 10 ml. and 0.1 ml. evaporated in the anode crater, before arcing at 10 amp. 0.01-10 mg. P per ml. can be determined. Konishi and Tsuge (1937) found a linear relationship between P content and line intensity between 0.2 and 8.0% P in plants. Brunstetter and Myers (1941) determined P in plant material, ashing it directly in a thin walled graphite electrode. P. H. Lundegårdh (1946 b) has discussed the possibility of the determination of P in plants by means of the intermittent d.c. arc. All the above methods used absolute density or line to background density ratios, without an internal standard. Norman and Johnson (1945) found that the limit of detection of the 2553.28A line varies with different matrices from 0.05 to 0.8 μg. on the electrode in a 15 amp., 3 mm. d.c. arc with the sample on the

cathode, illustrating the unreliability of a direct measurement without suitable internal standard.

Examples of arc determination of P in alloys are reported by Rollwagen and Ruthardt (1936) and Milligan and France (1941), sensitivities of 10-50 p.p.m. being obtained.

The high voltage a.c. arc would appear from the results of Owens (1938 a) and Ruehle and Jaycox (1940) to be more sensitive than the normal d.c. arc.

Rare Earths

Investigations on the rare earths by spectrographic methods cover a wider field than that covered in other groups of closely related elements. The spectral properties of the individual rare earths, unlike their chemical properties, vary very widely amongst themselves, so that the sensitivities range from high for elements such as Eu, La, Yb to rather low for Ce, Sm, and Gd. The sensitivity of the rare earths in the cathode layer arc has been discussed by Tongeren (1938) who draws attention to their tendency to produce sudden flashes of light in the arc column. The rare earths all fall into the group of rather involatile constituents, and show quite an appreciable cathode layer effect. In addition to the arc, determinations can be made in the spark, or in the flame, where certain elements are very sensitive. Apart from these standard line emission determinations, the emission of band spectra in the spark-in-flame or the flame around a heated carbon rod are possible methods, whilst bordering on spectrographic methods are those of infra-red photo-luminescence and the measurement of absorption bands in solution.

In the flame Lundegårdh (1934) has shown the great sensitivity of La 4378, 4403A, and Gd 4614, 5696A as well as the presence of bands due to many of the rare earths. The sensitivity of three lines of Eu 4594, 4627, 4661A has been pointed out by Piccardi (1933, 1937) whilst reference to the extensive work of Piccardi on the molecular emission spectra of the rare earths in the flame will be found in Piccardi (1939) where the fractionation of the rare earths is also discussed. Piccardi obtained the band spectra by spraying a solution into an oxy-coal-gas flame. Satisfactory qualitative and quantitative determinations of Sc, Y, La, Gd, Sm and Eu are possible. Plantinga and Rodden (1936) give 0.0001 M as the limit of detection of the band-heads of La, Y and Yb in a spark-in-flame source, using a hand spectroscope, by the method described earlier by Rodden and Plantinga (1934).

The determination of rare earths in ores, using an arc source, is described by McCarty, Scribner, Laurenz and Hopkins (1938) who applied 0.1 ml. of a nitric acid solution containing Mg or Zr as internal standard to a bored graphite cathode, which after drying was arced at 5.5-6 amp. for 30 seconds. Elements detected were La, Nd, Sm, Y, Gd, Dy and Yb, but no wavelengths are given. The wavelength range employed was 2500-3300A, with a Hilger

Large Quartz spectrograph. The determination of rare earths in plants in the arc, with carbon or copper electrodes, using a grating spectrograph, has been carried out by Scribner (1939), in connexion with the work on the high rare earth content of hickory leaves.

Borneman-Starynkevich, Borovick and Borovskii (1941) report the detection of rare earths in soils and plants, whilst Borovick (1937) and Borovick and Burova (1938) have worked with minerals. Bray (1942 a) draws attention to the high rare earth content of some titanites. Thoreau, Breckpot and Vaes (1936) studied the content in monazite.

Azcona (1941 a) has given a long account, which the author has not seen, of the spectrochemical properties of the rare earths, and Meggers (1941 c, 1942) has given the classification of the more important lines. Scott, at the Macaulay Institute, has found some difficulty in detecting traces of some of the rare earths in mixtures of others, from the table of wavelengths given by Harrison (1939 a). Thus it proved impossible to confirm the presence of a trace of Yb in Er, because Harrison records weak lines of the major constituent at the same wavelengths as the sensitive lines of the trace constituent. Scott has also observed some interference effects due to rare earths. 20% Er in a matrix of 95% Al_2O_3 and 5% Fe_2O_3 gave quite normal Fe intensities, whilst 20% Ho suppressed the Fe lines very appreciably. Gatterer and Junkes (1939) have determined Eu in Sm down to 5 p.p.m., with errors of $\pm 5\%$ at the 100 p.p.m. level, their technique following that of Scheibe and Rivas (1936) and involving the addition of solutions to both carbon electrodes which were burned in a long d.c. arc, with the spectrograms recorded by means of a glass spectrograph. The determination of La has been discussed by Bauer (1935) who took it as an example of a difficultly volatile element.

The spectrophotometric determination of some of the rare earths has been discussed by Rodden (1942) who gives transmittancies of the solutions at different wavelengths. Borovick and Burova (1937) determined Nd and Pr in minerals. Servigne (1939) reports the use of photoluminescence spectra of Pr and Nd for their detection in $CaWO_4$ phosphors. 5 p.p.m. of Nd gives a prominent series of lines at 8696-9124A and 10772-11188A.

Selenium

From the results of Feldman (1945), selenium would appear to be one of the elements most sensitive to changes in the base material in which it is being determined. Using 60 mg. of material in the graphite anode of a 10 amp., 6 mm. long, d.c. arc, of which the centre 2 mm. was utilized, he found that Se could not be observed in a SiO_2 matrix at 4%, but 0.1% Se as CuSe or PbSe in CuS or PbS could be observed by the 2413.5A line, whilst in a tellurium base Se was visible down to 0.01%. The addition of Te to sulphides caused a considerable enhancement, but not to MgO, KCl or $CaSO_4$ bases. A concentration method for Se (and Sb, As, Hg) is suggested whereby these elements are sublimed in a hard glass tube, then the sublimate

collected by melting a pellet of Te in the tube and bringing it into contact with all the wall surface. This pellet can then be analysed.

The Se line at 2413.5A is not the most sensitive, the strongest lines lying further in the ultra-violet, but is the line most suitable for normal spectrographic technique. Fenner (1939), determining traces of Se by means of the electrodeless ring discharge in a high frequency magnetic field, found 2164.3A stronger than 2413.5A (on Agfa Ultraviolet plates) for small traces, but the easily reversed 2164.3A was weaker when more Se was present.

Milbourn (1937) records the use of a small (Hilger E37) quartz spectrograph and Schumann plates for the detection of Se using the lines at 1960, 2040, 2063 and 2073A, 2040A being the most sensitive.

Reference to the spectrographic determination of selenium is made in papers by Kraemer (1934) and by Gerlach (1938) on the interrupted arc. There would appear to be no records of results of plant and soil analysis spectrographically, although the technique of Feldman is possibly applicable to samples from areas where selenium poisoning occurs.

Thallium

Thallium is sensitive in flame sources and when present in solution can be determined in the Lundegårdh flame in concentrations of 0.003-0.3% by the 3775.7A line, using Co 3873.1A as internal standard (Solodovnik and Gusyatzkaja, 1940). Lundegårdh (1934) gives the sensitivity limit for the 3775.7A line as 0.000002 M; 3519.2A, 0.0001 M; 5350.2A, 0.0005 M; 2767.9A, 0.002 M.

In the d.c. arc Tl behaves as one of the more volatile elements, falling off in intensity after the first minute in the cathode layer arc. By this method the Tl 2767.9A line is measurable from 100 p.p.m. upwards. Rusanov and Bodunkov (1938) used Fe 5270.4A as internal standard against Tl 5350.5A. Ahrens (1945 a, b) has been able to detect Tl in clays and minerals down to 0.3 p.p.m. in the d.c. arc, using the 3775.7A line, with CN bands suppressed by the addition of 5-10% KCl or alkali carbonates.

Most investigations of thallium have been to study suspected poisoning. Berge and Patzsch (1935) recovered Tl from tissue with HNO_3+HCl, precipitated with H_2S from alkaline solution in presence of Fe and examined the precipitate. A similar concentration method was used by Künkele (1938) and Tl in exhumed bodies was detected spectrographically by Böhmer (1938), mainly in lungs, liver and bones.

Symptoms of Tl toxicity in tobacco are similar to those of frenching but they are distinct phenomena (Shear and Ussery, 1940), as no evidence of Tl could be found spectrographically in frenched plants, but was easily observed in plants grown in Tl-treated media. Tl could be detected in ash samples in amounts less than 0.0001% from plants grown in nutrient solutions with only 0.016 p.p.m. Tl.

Tungsten

There are no reports of the presence of tungsten in plants or soils, although small quantities are undoubtedly present in the latter, and it is probably because the spectrographic sensitivity of tungsten is not great that it has not been observed. Lagrange and Tchakirian (1939) have reported its presence spectrographically in ashes of Lithothamnion, a calcareous alga. It has been suggested that it may play some part in nitrogen fixation (Bortels, 1938, 1940), resembling Mo and V in this respect.

Donati (1927) found that 0.01% WO_3 could be observed in the d.c. arc in an SiO_2 base. Tongeren (1938) gives a similar sensitivity value for the 4008.8A line, whilst Ahrens (1943 a) determines down to 0.03% WO_3 in siliceous material using the 2944.4A line in a 6.5 amp. carbon arc with Si as internal standard, with an accuracy of $\pm 6.5\%$ or better. Raichbaum (1939) used added Co as internal standard. Carlsson (1943) reported the determination of 0.01-0.25% to within $\pm 0.01\%$ in ores.

Although concentration methods for W have not been reported for soils, several methods used for rocks could undoubtedly be applied. Scobie (1943) precipitated it together with hydrated Al_2O_3 by means of $NaHCO_3$, getting down thereby to 0.0002% W in an ore, but Wilson and Fieldes (1944) pointed out that this method was satisfactory only with low Al_2O_3 contents, and preferred a precipitation of W with Ti by means of tannin and antipyrine. They used the 2947 and 2551A lines, arcing the precipitate in pellet form after addition of $(NH_4)_2SO_4$ at 3 to 7 amp. Their limit of detection was 0.00007% and the accuracy $\pm 25\%$. A concentration method, using α-benzoinoxime, for the determination of small amounts of tungsten in steels is described by Fischer, Spiers and Lisan (1944).

Tungsten behaves in the arc as one of the more volatile constituents and comes off during the early stages of the burning. It does not show a cathode layer effect. Donati (1927) has reported a depressing effect of Mn on the intensity of the W lines.

Chapter 11

PREPARATION OF SOILS, PLANTS AND OTHER MATERIALS

It is essential that the requisite precautions to avoid contamination of samples intended for spectrographic analysis should be observed at all stages of sampling and pre-treatment. It is remarkable how often samples of soils, plant materials or other biological samples, intended for trace element determinations, are packed in metal containers without regard to the possible contamination effects. An example of this difficulty may be instanced where abnormally high Sn content of sheep ticks was traced to their having been collected in a tinned metal box. Mutual contamination of soil and plant material must also be avoided. Quite useless samples of plant materials have been received in which the plant had been pulled up by the roots and then folded so that foliage and soil-carrying roots were in contact. It has been found advisable to recommend cutting of plant samples, rather than plucking, recommended by the Agricultural Education Association (1943), as this appears to reduce the risk of contamination, which is a major difficulty especially in plants of low habit. Soils can be safely sampled by an iron auger. Both plants and soils should be placed in clean paper-lined bags for transport to the laboratory.

a. Soils

Soils should be air dried on trays of material which cannot cause appreciable contamination. Zinc, galvanized iron, copper, brass and similar materials should be avoided. Aluminium or non-metallic trays should be employed, with a paper lining which is renewed for each sample. The soil sample which is used as the basis of most investigations comprises only the material passing a 2 mm. sieve, and here again care must be taken to avoid contamination. Aluminium would again probably provide the most satisfactory material. For the determination of the total contents of trace constituents, the 2 mm. sample should be quartered to give a 20 g. aliquot, which is ground in a mechanical agate mortar for 30-60 minutes to about 100-mesh size. The Morrice mechanical pestle and mortar of T. Dryden and Sons, Ltd., has proved very satisfactory. Before filling into electrodes, finely ground soil material is ignited at 450°C. to destroy organic matter, which can interfere with the burn.

For the determination in soils of the amounts of trace constituents that are available to the plant, all the methods so far employed must be considered to be tentative, as the data which are available up to the present

are, for most elements, quite inadequate to allow of conclusions to be drawn regarding the relationship of solubility to plant uptake.

A convenient extractant is 2.5% acetic acid (approx. N/2 ; pH 2.5) similar to that employed for the determination of easily soluble P_2O_5 and K_2O at the Macaulay Institute. 20 g. of soil (<2 mm.) are shaken overnight on an end-over-end shaker with 800 ml. of 2.5% acetic acid. The overnight period of shaking is adopted for convenience and other durations might be equally suitable. The extract is filtered through an 18.5 cm. Whatman 530 filter paper, soil and paper washed with distilled water and the extract evaporated to dryness, first to low bulk on an electric hot plate (Simmerstat control) and finally on a steam bath. The residue, still in 1000 ml. Pyrex beakers, is treated with Analar H_2O_2 on the steam bath to remove organic matter. The quantity required depends on the soil, but is generally of the order of 3 or 4 additions of 5 to 10 ml. The residue is taken up in 50 ml. of 1 : 2 hydrochloric acid and filtered through 9 cm. Whatman 41 filter papers. 10 ml. of an Fe solution in hydrochloric acid, equivalent to 2 mg. of Fe_2O_3, and free from trace constituents, are added and the whole is diluted to 150 ml. for the concentration process described below. Dilute acetic acid extracts little more than traces of Fe (0.1-0.5 mg.) from most soils (some organic soils contain more soluble iron) so that the addition of Fe for use as internal standard is necessary.

For certain elements, such as Mo, a larger quantity is extracted by a neutral or alkaline extractant, and a suitable solution is neutral normal ammonium acetate, prepared by mixing the required amounts of ammonia and acetic acid and taking to pH 7. 20 g. of soil are either leached to one litre or extracted with 800 ml. of ammonium acetate and then treated as above. As the process is arbitrary, there seems little to choose between extraction and leaching. Generally the shaking extraction technique has been employed.

Oertel (1944 b) has described the preparation of extracts of soils with constant boiling HCl. 10 to 20 g. of soil is treated with 35 to 70 ml. of acid in a digestion unit of Pyrex glass, comprising a conical flask with a ground-in condenser tube, for 48 hours on a water bath. Internal standards are added to the soil prior to extraction. Because of difficulty in dealing with evaporated residues of soil extracts, owing to such factors as fractional crystallization and deliquescence, the liquid extract is added dropwise to a graphite electrode from a dropping bottle. The electrodes are then dried on a specially controlled hotplate. No information is given regarding subsequent spectrographic technique or elements determined.

In all such extraction methods it is essential to employ reagents which are free from the trace constituents concerned, and methods of purification are discussed in a subsequent section (see p. 128).

The use of the Lundegårdh method for the determination of alkalis, alkaline earths, magnesium and manganese in soil extracts and plant materials has already been described (see p. 49) so that it is unnecessary to repeat the extraction details here.

b. Plant Material

Plant material is dried at 80°C. in an electric oven—a copper lined oven should be avoided—and then ground in a Christy and Norris Hammer Mill. This may introduce a slight iron contamination, but appears to be more satisfactory than other methods. The problems involved in the grinding of plant materials are discussed by Piper (1942) and Hood, Parks and Hurwitz (1944).

For the direct examination of plant ash, about 1 g. of oven dry material is ashed overnight at 450°C. in a silica crucible in an electric muffle furnace. This ash is then treated in the normal manner for spectrographic analysis.

When chemical concentration of the trace constituents in plant materials is required, a larger sample is necessary and the practice at the Macaulay Institute is to ash 20 g. of oven dry material overnight in a platinum basin. The most satisfactory ashing temperature has been found to be 430-450°C., in a silica-lined electric muffle furnace, with a loose silica lid over the basin. A slight current of air should be drawn through the furnace during the early stages of the ignition to prevent deposits of carbon and tarry material from choking the flues. This method gives satisfactory ignition of finely ground herbage, straw, grain, turnip leaves and bulbs, and potato tubers.

The ash is transferred to a platinum crucible and mixed with 4 g. of purified anhydrous Na_2CO_3. After fusion, the melt is dissolved in 50 ml. of 1 : 2 HCl, evaporated to dryness on a steam bath and taken up again in 50 ml. of 1 : 2 HCl. The SiO_2 present is filtered off on a 9 cm. Whatman 41 filter paper and washed with hot water. The filtrate is made up to 150 ml. and is then ready for the concentration process. The necessary additions of Al and sometimes Cd are detailed in the description of the concentration process.

The fusion process for the extraction of the trace constituents from the ash has been adopted in preference to an acid extraction because of the danger of incomplete extraction by the latter. Evidence has been obtained of complete recovery of additions of Co, Ni, Mo, Cr, V, Sn, Pb, Ti and Zn made to the ash before fusion (Mitchell and Scott, 1947). Several workers have preferred a wet-ashing process, but this is more suitable for smaller amounts than the 20 g. samples which have been found necessary for elements, such as Co, present in very small amounts. Cholak and Hubbard (1944 b) use $H_2SO_4+HNO_3$, supplemented by $HClO_4$, to ensure complete solubility of the alkalis and alkaline earths, which they state are incompletely extracted by acids after dry ashing. Cholak and Story (1941) find that such elements as Mn, Pb, Sn, Al, Cu, Ag, Fe and Tl can be determined in biological materials after dry ashing at 500°C., as there is no loss during the ashing process. A somewhat lower temperature, of about 450°C., is generally considered advisable for Zn. Piper (1942) gives a full discussion of different wet and dry ashing techniques for plant material.

c. Rocks and Minerals

Rocks have to be broken down previous to grinding, and the procedure must be chosen to avoid contamination with elements which are to be determined. Whilst it is occasionally impossible to avoid employing a diamond mortar, some types of steel are much more dangerous than others, and the possibility of contamination must be kept in mind. It seems possible that quenching of heated crystalline rocks in cold water will simplify the process of disintegration. Granites so treated can be broken down by hand in a large agate mortar.

Minerals, which are generally obtained by hand-picking, magnetic separation and heavy liquid separation from powdered rocks, are liable to contamination in the process unless stringent precautions are taken. The use of methylene iodide, stabilized by tin, as the heavy liquid should obviously be avoided.

Fertilizers can generally be used either directly or after grinding in an agate mortar. Neither rocks, minerals nor mineral fertilizers require to be ignited after the final grinding.

The spectrographic procedure chosen for the determination must depend on the object in view. For most purposes, the semi-quantitative cathode layer arc technique is adequate, the samples being mixed with carbon powder and filled into electrodes in the usual manner. Rankama and Joensuu (1946) point out the advantage of increasing the carbon : sample ratio to 4 : 1 and including also 1 part NaCl with certain types of minerals, such as titanite. The grinding of solid samples, as well as the problem of sampling and mixing, is discussed by Ballard, Oshry and Schrenk (1943) and Lykken, Rogers and Everson (1945).

d. Concentration Methods

For the determination of trace constituents in many types of biological materials, it is necessary to remove the large bulk of diluent material, such as alkalis, alkaline earths and phosphate in plant materials, and alkalis and alkaline earths in soil extracts, in order to reach a concentration of trace constituents within the sensitivity range of the spectrographic method employed. At the same time the use of a concentration method can be of value in circumventing the effects of variation in composition of the sample compared with that of the standards, and in permitting the introduction of an internal standard. Disadvantages of a concentration method include the increased time and material required for the determination and the possibility of contamination occurring during the chemical process. By careful choice of reagents and their purification, the latter effects can be reduced to negligible proportions for most elements.

Concentration methods can be divided into two rather distinct categories, firstly those which are non-specific, the aim being to concentrate as many trace constituents as possible with the simultaneous rejection of all the unwanted major constituents, and secondly those which deal with

one or a few specific elements which it is desired to determine. For the latter, the usual methods of chemical separation may be applicable, but for the former the problem is rather different from that generally dealt with in analytical chemistry. The concentration of as many trace constituents as possible is obviously desirable in surveys of the influence of trace constituents in biological work, and it is along this line that the concentration work at the Macaulay Institute has been developed.

A preliminary survey of the properties of the various types of reagent available suggested that an organic reagent would be most suitable, and from those with which preliminary experiments were carried out (including also cupferron, anthranilic acid, pyrogallol, quinaldinic acid, α-nitroso-β-naphthol, tannic acid and thionalide) it was found that 8-hydroxyquinoline was most suitable. The technique adopted is to precipitate the trace constituents on a carrier precipitate of Al and Fe quinolates at pH 5.1 in a solution buffered with ammonium acetate. Quantitative recovery of Co, Ni, Mo, Cu and Zn was reported by Scott and Mitchell (1943) whilst further work has indicated (Mitchell and Scott, 1947) that Ti and probably Ga and Tl are also quantitatively recovered whilst Cr, V, Ag, Sn, Pb, Ge, Be and Cd are not completely precipitated. As the method has proved of practical value for the determination of Co and Mo in soil extracts, plant materials and animal organs, details of the procedure will be given before considering a development, employing mixed organic reagents, which extends considerably the number of elements recovered.

The solution containing the trace constituents and the unwanted alkalis, alkaline earths and phosphate should be about 150 ml. in volume and contain some 15 ml. of concentrated HCl. The solution should contain Al equivalent to about 30 mg. of Al_2O_3 and Fe equivalent to 2-5 mg. of Fe_2O_3. It is generally necessary to add Al to plant extracts and Fe to acetic acid extracts of soils, but only experience can determine the additions necessary with different types of material. In the initial description of the method Al was not added, but it has been found more convenient to make the addition at this stage. A 5% solution of 8-hydroxyquinoline in 2N acetic acid (114 ml. of glacial acetic acid per litre) is now added, 10 ml. being sufficient for plant materials and most soils, but it is advisable to add 15 ml. to soils, which occasionally contain considerably more than 40 mg. of Al and which require more precipitant. 1 : 1 ammonia is now added drop by drop until the colour of the solution just changes from yellow to emerald green (due presumably to an 8-hydroxyquinoline-iron complex) at a pH of 1.8-1.9. This colour change allows the pH of the solution to be established and so enables accurate buffering to the final pH of 5.1-5.2, which is produced by the addition of 50 ml. of 2N ammonium acetate. The solution is stirred vigorously and set aside overnight at room temperature, then filtered through 9 cm. Whatman 540 filter paper and washed with cold water. After partial drying, the precipitate is ashed with the paper in a small porcelain crucible in an electric muffle furnace at 450°C. An easily manipulated ash, which does not adhere to the crucible, is obtained. It is transferred to glazed paper and weighed on an Oertling torsion balance, after it has had

time to come to air dry moisture equilibrium (1-2 hours in the balance room). The precipitate should weigh 30-50 mg. If below 30 mg. it can be made up to about 40 mg. by addition of pure Al_2O_3 powder. The ash is thoroughly ground in a small agate mortar and is then ready for spectrographic determination of the trace constituents (requiring up to 15 mg.) and for colorimetric determination of Fe_2O_3 content (5-10 mg.).

The incomplete recovery of such trace constituents as Pb, Sn, Cr, V and Cd by the straight 8-hydroxyquinoline precipitation and the rather unsatisfactory determination of Zn with Fe as internal standard led to further investigations into the use of mixed precipitants to bring down these elements. The very satisfactory properties of 8-hydroxyquinoline, as far as handling of the precipitate and pH control of the solution were concerned, led to its retention as the main precipitant, with small additions of other reagents in an attempt to bring down the other trace constituents. It has been found (Mitchell and Scott, 1947) that a mixture of 8-hydroxyquinoline, tannic acid and thionalide gives complete recovery of Co, Ni, Mo, Cr, V, Be, Ge, Sn, Pb, Ti, Zn and Cd, and probably also of Ga, Tl and Ag, although these elements have not been completely studied from the spectrographic aspect. The results of determinations for these three elements are invariably much too high. Table 5 from Mitchell (1946) indicates the recovery from standard solutions by concentration followed by spectrographic analysis by the variable internal standard cathode layer arc method. The results quoted are the means of closely agreeing duplicates. The errors of the whole process will be seen seldom to exceed $\pm 10\%$ over the range of contents shown. A content of 50 p.p.m. in the precipitate corresponds to 2 micrograms in the solution, or, with the normal aliquots, one part in ten million in the plant material or soil. By the concentration process a 500- to 1000-fold concentration can be effected. The amount filled into the electrode is about one-tenth of the precipitate, or 0.2 μg. upwards. For Co, amounts as low as 0.04 μg. can be determined with errors of the $\pm 10\%$ order (Scott, 1944).

The procedure for the precipitation with mixed reagents follows that for 8-hydroxyquinoline alone as far as the neutralization with ammonia (1 : 1) to the emerald green colour change at pH 1.8-1.9, except that to the solution are added also 10 ml. of a solution containing 0.4 mg. of Cd as $CdCl_2$. Thereafter 30 ml. of 2N ammonium acetate are added, and, after stirring, 2 ml. of 10% tannic acid in 2N ammonium acetate, and 2 ml. of 1% thionalide in glacial acetic acid, followed immediately by an equivalent quantity of ammonia, with stirring. The amount of ammonia equivalent to 2 ml. of glacial acetic acid is previously determined by titration with bromthymol blue as indicator. It is convenient to add this ammonia in a volume of 20 or 25 ml. Tannic acid and thionalide should be freshly prepared.

After standing overnight, the precipitate, which is slightly more voluminous than that with 8-hydroxyquinoline alone, is filtered through 11 cm. Whatman 540 filter paper and, after drying, ashed as before in a porcelain crucible at 450°C. The ashed precipitate is again quite free and simple to manipulate.

TABLE 5

Concentration from Standard Solution with 8-Hydroxyquinoline + Tannic Acid + Thionalide followed by Spectrographic Analysis

Parts per Million					
Present	Found				
	Co	Ni	Mo	Cr	V
50	47	52	57	50	53
125	126	135	124	126	127
250	249	272	241	235	244
500	471	520	503	432	497
1250	1290	1375	1120	1220	1175

Parts per Million						Per cent	
Present	Found					Present	Found
	Be	Ge	Sn	Pb	Ti	%	Zn
100	117	162	—	—	110	—	—
250	255	269	295	—	—	0.5	0.56
500	490	525	537	544	542	1.0	1.02
1000	1023	1014	1088	956	1100	5.0	5.07
2500	2660	2870	2340	2611	—	10.0	10.16
5000	—	—	—	—	5435	—	—
1%	—	—	—	—	1.07%	—	—

The recovery of those of the trace constituents other than lead which are not precipitated by 8-hydroxyquinoline alone is effected by the tannic acid, whilst thionalide precipitates the lead. It has been found, however, that tin results are more reliable in the presence of thionalide.

The addition of Cd is made to provide a second internal standard for Zn determination. The comparison of the volatile Zn with the relatively involatile Fe caused some irregular results to be obtained when there was any disturbance in the burning of the arc. A slight splutter and loss of material cause high results to be obtained for such elements as Zn and to a smaller extent Sn and Pb. This is, as already indicated, presumably because the emission of these elements is more intense in the arc column which contains no other metallic constituents, and for a time after a splutter only the volatile constituents enter the arc column. Correct results are obtained by Zn/Cd comparison but not by Zn/Fe under such conditions, the latter being too high. If the same value is obtained by both methods, it is an indication of a good burn, not only for Zn, but also for other elements

intermediate in volatility between Zn and Fe. When a known amount of Cd is used as internal standard, the precipitate weight is employed as the measure of the variable internal standard content.

The tendency of the precipitates from the mixed reagents to splutter is diminished by increasing the carbon : sample ratio from equality to 2 : 1 and at the same time using an electrode with a bore of 1.0 mm. (drill No. 61) in place of the usual 0.8 mm. bore. With this size of boring the weight of sample introduced into the electrode is kept at the previous level of 3 to 4 mg. It is desirable to prepare a working curve with the same type of electrode, although for Co and a few other elements, no significant shift of the working curve as a result of changing the carbon : sample ratio has been observed. The cause of the increased tendency to splutter with the precipitate from mixed organic reagents has not been ascertained. It is most liable to occur with plant materials, and it is possible that the sulphur content of the thionalide may be involved.

These concentration methods are now being employed as the standard procedure at the Macaulay Institute for the determination of trace constituents in acetic acid and ammonium acetate extracts of soils, and in ashes of plant materials and animal organs.

It is important to avoid the introduction, from laboratory equipment or from reagents, of any of the elements being determined. Ignitions are carried out in a silica muffle furnace, in platinum, silica or good quality porcelain. The water baths employed are of stainless steel protected by a plastic resin paint (Townson and Mercer T & M S88), fitted with tops of toughened plate glass (Pilkington) or unplasticized Perspex, with porcelain rings or Perspex lids. Heating is by means of 1250 or 1500 watt electric kettle immersion heaters, controlled by Sunvic Simmerstats and hot wire vacuum switches. Metal in the laboratory is protected as far as possible by T & M S88 paint, and all vessels are kept covered from dust whenever possible.

Acetic, nitric and hydrochloric acids (Analar grades) are redistilled in all-glass stills before use, whilst ammonia is purified by reabsorption in distilled water, and kept in waxed bottles. It has been found that Analar grades of these reagents, used in normal quantities in the above concentrations, can contribute considerably more of such constituents as Ni and Mo than do the materials being analysed, so that purification is necessary. B.P. grade may sometimes be purer, as far as trace constituents are concerned, than Analar, but each batch must be tested and it is more satisfactory to purify all materials used. Normal reagent grades of 8-hydroxyquinoline, thionalide and tannic acid are suitable. Pyrex and Phoenix glassware is employed throughout. For handling crucibles and basins, platinum tipped tongs are employed, whilst spatulas should be of platinum, aluminium or non-metals.

For certain samples, such as ash of blood, difficulty is experienced owing to the very high Fe content, and a further pre-treatment process has

had to be introduced to remove this. The method employed has been to extract the Fe from a hydrochloric acid solution (60% HCl) of the sample by means of ether, then to proceed as detailed above, adding a small amount of iron to serve as internal standard.

A similar concentration method, employing isopropyl ether to remove Fe from solutions of iron and steel prior to trace element determination has been given by Wolfe and Fowler (1945). Results are given for Al, Bi, Cd, Cr, Co, Cu, Pb, Mg, Mn, Mo, Ni, Ag, Sn, Ti, V and Zn, some of which show evidence of slight loss due to solubility in ether. Mo is less soluble in isopropyl ether than in ethyl ether. In the latter As, P, Sb and Sn are stated to be partially soluble, Cu, Zn and V very slightly soluble and Al, Ag, Bi, Ca, Cd, Cr, Co, Pb, Mn, Ni, Ti, W and Zr totally insoluble. Wolfe and Fowler analysed the concentrate in solution, employing the high voltage a.c. arc.

A widely employed concentration technique covering a number of elements is electrolytic deposition, although few quantitative results on recovery are available. The method has been used by Bayle and Amy (1927, 1928) for Au, Ag, Cu, Pb, Sb, Cr, Mn, Co and Ni, generally in pairs or separately, by deposition on a Cu or Zn cathode. Riedl (1932) reports increased sensitivity for Sb, As and Te by electrolytic concentration. Schleicher, in a series of papers, has reported the concentration of many constituents of mine waters and similar materials on an amalgamated Cu wire (Schleicher, 1933, 1935, 1937 ; Schleicher and Brecht-Bergen, 1935 a, b ; Schleicher and Kaiser, 1936 ; Schleicher and Laurs, 1937). Schleicher and Kaiser found Ag, Cu, As, Bi, Sb, Te, Hg, Pb, Sn, Cd, Ni, Co, Zn, Fe, Ga, W, Tl, Mo, Al, Cr and Mn in a mine water, whilst Schleicher and Laurs included also Ca, Ba, Sr, Mg, Na, Li, Rb and Cs. Sannié and Poremski (1939) determined small amounts of Ni, Zn, Pb and Hg by micro-electrolysis followed by spectrographic analysis. Gerlach and Schweitzer (1930 b) investigated the recovery of Hg on Sn foil, and Urbain (1930) that of Au from Ag on carbon rods. Schwarzacher (1931) has discussed the application of micro-electrolysis followed by spectrographic analysis to biological materials.

Amongst other organic reagents which have been employed is cupferron, by Baudisch (1935) for Fe, Cu and Ti, and by Strock and Drexler (1941) for Ti, V and Zr. Dithizone is used by Rohner (1938) for Cu, Ag, Au, Zn, Cd, Hg, Tl, Sn, Pb, Bi, Mn, Co, Ni and Pd. Hibbard (1938) reports a concentration of Cu, Zn, Co and Ni by means of dithizone from soil extracts in a non-spectrographic method, whilst Heller, Kuhla and Machek (1935) have used the same reagent for Cu, Bi, Pb, Cd, Zn, Ni and Co in waters. Cholak and Hubbard (1944 a) concentrated Cd by means of dithizone. Concentration by means of an extractant such as dithizone is particularly suited to spectrographic methods like the high voltage a.c. arc in which the electrode is treated with a few drops of solution.

The most popular inorganic reagent would appear to be H_2S or in some instances ammonium sulphide. Vanselow and Laurance (1936) determined

Zn in plant material with Cd as carrier precipitate, Harper and Strafford (1942) As, Pb, Cu, Sb and Sn in pigments, and Steadman and Thompson (1941) Bi in biological material. Geilman and Brünger (1931) used H_2S for Ge, Cruse and Schubert (1936) for Pb in blood, it being first precipitated as sulphide and then deposited electrolytically, Berge and Patzsch (1935) for Tl in tissues, and Rice (1938) for Pt metals and Re in ores. Amongst those using ammonium sulphide are Siemeister (1936) for Ni, Co, Mn and Cr in minerals, and Strock and Drexler (1941) who give recovery percentages of 55% for Ni, 84% for Co and 13% for Mn after ammonium sulphide precipitation of 0.0125-0.125 mg. in the presence of 25 mg. of Fe. Ernst and Hörmann (1936) determined Ni in sea water after ammonium sulphide, and V and Mo after ammonia, precipitation.

Amongst co-precipitation methods Park and Lewis (1933) and Breckpot (1934) concentrated Sb from Cu by means of MnO_2, whilst Breckpot (1935 a, b) employed $Fe(OH)_3$ as carrier precipitate for Bi, As, Sb, Sn, Pb and Ge in a solution of electrolytic Cu metal. Breckpot (1935 d) used a combined $Fe(OH)_3$ and H_2S process. Pb was determined by Rosenqvist (1942) by co-precipitation with $SrSO_4$ from extracts of silicate rocks, and by Park and Lewis (1935) by precipitation with $Na_2HPO_4+(NH_4)_2CO_3$. Wilson and Fieldes (1942 b) concentrated Sr with Ca as oxalate.

Tungsten has been concentrated by Scobie (1943) by precipitation along with Al_2O_3 by means of $NaHCO_3$. Fischer, Spiers and Lisan (1944) employed α-benzoinoxime, whilst Wilson and Fieldes (1944) recovered Ti and W by tannic acid and a mixed reagent containing antipyrine and cinchonine in acid solution.

Concentration by means of sublimation in a sealed tube at 1200°C. has been employed by Rose and Böse (1935) for Zn, Ga, Ag, Ti, Mn, Cu and Fe, and by Feldman (1945) for Se.

The so-called pyroelectric concentration method (Rubies and Doetsch, 1934; Rubies and Azcona, 1936) makes use merely of differential volatilization in the arc. The method of Preuss (1939), which employs a large amount of material in a heated chamber and feeds the vapours to the electrode, can however be considered to be a concentration method. Bertrand (1946) has described a method for Rb in K salts in which a horizontal carbon arc is struck in a small furnace containing the sample.

Adsorption of the unwanted or wanted constituents by means of an exchange active plastic resin may provide sufficient concentration or removal of unwanted constituents, as found by Eastmond (1946) for the determination of Ca in microbiological culture media.

e. Determination of Iron in Concentrates and Other Samples for the Variable Internal Standard Method

For the variable internal standard method, using Fe as the internal standard, it is necessary to know the Fe content of the material taken for analysis. In the concentration method the total amount available may be

30 mg. or less, so that it is necessary to employ for the determination of Fe a method requiring only some 10 mg. That adopted has been described by Scott (1941 a) and Scott and Mitchell (1943) and employs the purplish or amethyst colour produced by Fe in the presence of sodium salicylate in acetic acid solution.

To determine the Fe_2O_3 content of concentrates or other samples, such as finely ground soils, containing 3-15% Fe_2O_3, 5-10 mg. are weighed on a micro-balance into a 10 ml. platinum crucible. As an accuracy of 0.01 mg. is more than adequate, the weighing is very quickly performed. About 100 mg. of Na_2CO_3 are added and the contents of the crucible well mixed with a platinum wire. After fusion for about one minute (or longer with silicates) and cooling, the melt is dissolved in 10 ml. of 1 : 1 hydrochloric acid. Any silica present should go into solution. The whole is transferred without filtration to a 50 ml. graduated flask, a 20 ml. aliquot is pipetted into a second 50 ml. graduated flask and 5 ml. of 1% sodium salicylate added. 1 : 1 ammonia is added drop by drop until the reddish colour first obtained turns yellow, then two drops in excess. 1 : 1 acetic acid is now added, first until a reddish colour reappears, then a further 5 ml. The volume is now made up to 50 ml. with distilled water and the density of the amethyst colour measured immediately on a Hilger Spekker Absorptiometer using No. 5 green filters, adjusted to a distilled water calibration value of 1.00. The values obtained are converted to Fe_2O_3 content by reference to a curve obtained from similarly treated standard solutions prepared from ferric ammonium sulphate (0.604 g. per litre is equivalent to 0.1 mg. Fe_2O_3 per ml.). A range of 0.05 -0.50 mg. Fe_2O_3 in the final 50 ml. is covered, and is suitable for Fe_2O_3 contents of 3-15% in 40 mg. concentrates using 5-10 mg. per determination. The absence of serious interference effects has been demonstrated by Scott (1941 a) who obtained results reproducible to 1% with pure solutions. A set of 6 samples can be weighed out, fused, dissolved and determined in little over 2 hours.

f. Purification of Chemicals and Ingredients of Standard Mixtures

The purification of reagents for use in spectrographic work has been discussed by Hughes (1943). He recommends distillation for HCl, HNO_3, and NH_4OH. H_2SO_4 is reported to be pure as bought. Pure H_3PO_4 is prepared from sublimed P_2O_5. SiO_2 is obtained from $SiCl_4$ by fractional distillation. Hughes found difficulty in removing Sr and Ba from Ca compounds, recommending repeated crystallization of Ca oxalate or $CaSO_4$. Methods are also given for preparing pure Mg, Na and K compounds. Distillation is most efficient, followed by extraction processes, whilst recrystallization is least efficient.

The purification of chemicals from trace constituents has been discussed by Piper (1942) and Stiles (1946) where further references are to be found, especially to the preparation of pure culture media.

Some of the methods which have been employed at the Macaulay Institute are as follows :

Sodium Carbonate Na_2CO_3. To prepare anhydrous sodium carbonate suitable for the fusion of plant ash it is generally necessary to remove Pb, Sn, Ni and Fe, which are frequent impurities observed in most grades of Na_2CO_3 and $NaHCO_3$, including Analar and B.P. The procedure adopted for purification is as follows : 200 g. of Na_2CO_3 are dissolved in one litre of hot distilled water and filtered through an 18.5 cm. Whatman 530 filter paper. The filtrate is extracted 3 or 4 times with 50 ml. of 0.01% dithizone in $CHCl_3$, then washed 3 times with 50 ml. $CHCl_3$. $Na_2CO_3.10H_2O$ is got out of solution by cooling with an ice-salt freezing mixture. It is filtered off on a 15 cm. Whatman 530 paper in a Buchner funnel and allowed to effloresce on a clock glass in a drying frame at 25-30°C. After efflorescence to $Na_2CO_3.H_2O$ is complete, Na_2CO_3 is obtained by ignition at 300°C. Material so prepared has been found to be satisfactory for most trace constituents, giving very small blanks.

Silica SiO_2. The starting material was naturally occurring crystal quartz, selected pieces of which were first broken up, and finely ground in a mechanical agate mortar. The initial disintegration is facilitated by heating the quartz to 500-600°C. and then quenching in cold water, after which it is easily powdered. The powder is extracted several times with HCl (Analar, redistilled from glass : constant boiling) and finally with glass distilled water. The silica so obtained was pure except possibly for a trace of Zr.

Alumina Al_2O_3. The best starting material was found to be B.P. grade aluminium sulphate. This was dissolved in distilled water, filtered and $Al(OH)_3$ precipitated in boiling solution with redistilled NH_4OH. The precipitate was filtered off, washed and redissolved in 6N HCl. Ether-soluble impurities such as Fe, Ga and Mo were then removed by shaking 3 times with ether, after which $Al(OH)_3$ was precipitated by NH_4OH once more, washed with boiling water, filtered and ignited to Al_2O_3.

Ferric Oxide Fe_2O_3. This is prepared from $FeCl_3.6H_2O$ (Analar) by dissolution in 6N HCl, and extraction by shaking with an equal volume of ether. The ether layer is then extracted once with water and the Fe precipitated from the water layer by means of NH_4OH, filtered, dried and ignited to the oxide. The product is free from Co, Ni, Cr, etc., but starting material free from Mo and Ga should be selected.

Calcium Oxide CaO. Farmer (1946) has prepared Sr- and Ba-free CaO in the following manner. : 10 g. of $CaCO_3$ are dissolved in 35 ml. of constant boiling HCl and the solution neutralized with NH_4OH. 200 ml. of R.S. alcohol are added and group 3A metals filtered off after coagulation on the water bath. The solution is then made just acid with HCl and 15 g. 8-hydroxyquinoline in 200 ml. R.S. alcohol added. This solution is warmed and about 25 ml. 1 : 1 NH_4OH slowly added. The precipitate is filtered hot after not more than 5 minutes standing and washed by mixing to a paste with alcohol in a beaker and treating with hot water, then refiltered.

(After cooling, the mother liquor gives a further precipitate which contains considerably more Sr.) The precipitate is ignited at 450°, dissolved in HCl and the solution made alkaline with NH_4OH and filtered. From this solution, made strongly alkaline with NH_4OH and heated nearly to boiling, $CaCO_3$ is precipitated by passing in CO_2, and CaO is obtained by ignition.

Magnesium Oxide MgO. Specpure grade is satisfactory.

Potassium Sulphate K_2SO_4. Sulphuric acid was added to a KOH solution and evaporated till surface crystallization began. The crop of crystals obtained on cooling was removed and the remainder of the K_2SO_4 obtained from the solution. Sr present in the original KOH was concentrated and removed in the first fraction.

Titanium Oxide TiO_2. Reagent grade is satisfactory, but individual lots must be tested to ensure this.

Chapter 12

THE APPLICATION OF SPECTROGRAPHIC METHODS TO THE ANALYSIS OF SOILS, PLANTS, FERTILIZERS AND OTHER BIOLOGICAL MATERIALS

a. Soils and Soil Parent Materials

Soil analysis by spectrographic methods has developed along two distinct lines, namely the determination of the total contents of trace constituents in the soil, often by semi-quantitative methods to an accuracy of ±30-50%, and the quantitative determination of the amounts of soil constituents, both major and trace, removed from the soil by various extraction methods.

(i) *The distribution of trace constituents in soils*

One of the earliest comprehensive surveys of trace constituents present in soils (in Florida) is that of Rogers, Gall, Gaddum and Barnette (1939) who stated contents for the elements observed, namely Sr, Ba, V, Cr, Mn, Zr, Ni, Ag, Ti, Cu, B and Zn as ranges within the limits of which the actual content lay. The ranges chosen were

0. not detected
1. <0.001%
2. 0.0008-0.003%
3. 0.001-0.005%
4. 0.003-0.008%
5. 0.005-0.01%
6. 0.008-0.03%
7. 0.01-0.05%
8. 0.03-0.08%
9. 0.05-0.1%
10. 0.08-0.3%
11. >0.1%

The contents for the trace constituents detected, including Co and Pb data from Allison and Gaddum (1940), covered the following ranges :

Sr	0—11	Ag	0— 1
Ba	0—10	Ti	2—11
V	0— 6	Cu	0—10
Cr	0—10	B	2— 8
Mn	0—11	Zn	1— 7
Zr	2—11	Co	0— 4
Ni	1— 6	Pb	0— 4

Co and Pb were not found in any of the soils from Florida, but only in soils of other states. Tl, Li, Cs, Y, W, La, Sn, Cd, Be, Bi, Sb and As were looked for, but not observed in any of the samples. It is unlikely that all these elements are absent from Florida soils, but the fact that they were not observed indicates merely that they were below the spectrographic sensitivity for the wavelength region employed. Mitchell (1944) has quoted, for soils from North-east Scotland, figures of much the same order with contents in p.p.m. as follows :

Ag	up to 2	Mo	up to 2
Ba	300—5000	Ni	5—2000
Co	up to 300	Pb	up to 1000
Cr	10—5000	Rb	100—2000
Cs	up to 500	Sn	up to 200
Cu	5—5000	Sr	50—5000
Ga	5—300	Ti	1000 upwards
Ge	up to 10	V	20—1000
La	up to 500	Y	up to 500
Li	30—5000	Zn	not determined
Mn	200 upwards	Zr	50—1000

The Th upper limit of 1000 p.p.m. previously given was too high, owing to a coincidence with a Zr line, whilst Zn data are not available as the wavelength region covering the sensitive Zn line in the ultra-violet has not been employed.

There is little fundamental difference in the methods of stating the results adopted by Rogers and by Mitchell, who quotes the most probable content, when it is realized that a semi-quantitative figure actually indicates a range of at least $\pm 30\%$ around the value given.

Guelbenzu, Ruiz and Azcona (1944) found Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Si and Ti in some quantity in all the Spanish soils which they examined, whilst Ba, Be, Co and Sr were present in all near the limit of sensitivity. Li, Pb and V were observed in some 80% of the soils. Content ranges in p.p.m. were

Cu	100—1000	Sr	c. 1000
Ni	10—500	Ti	1000—10,000
Pb	1—10	V	1—100

An unusually high sensitivity for Be is reported by these workers.

The figures quoted for the total contents of trace constituents in soils indicate the levels which are to be expected in most soils. The significance of a total content in a soil is not particularly high, but it is probably greater for trace constituents than for major constituents, which seldom vary more than five to ten fold, whilst trace constituents may vary by amounts as great as one thousand fold from soil to soil. A semi-quantitative examination can often indicate the presence of an excessive content of a trace constituent, although deficiencies can seldom be detected thus. The low significance of the total content as far as practical applications are concerned, together with the large variations which are found, generally renders a semi-quantitative determination adequate.

Numerous other workers have reported determinations of total contents of one or more elements, either by a semi-quantitative or a more accurate quantitative method. In a series of papers, Pelisek has dealt with the occurrence of trace constituents in the soils of the Moravian province of Czecho-Slovakia, discussing also the distribution of trace constituents in the profile. The occurrence of Ga was reported by Pelisek (1940 a) in all soils examined except magnesium-rendzina soils on serpentine. The Ga content appeared to follow that of Al, and Ga was leached from the A_1 and A_2 layers of podzols, whilst the B horizon was a zone of Ga accumulation. This translocation could not be observed in chernozems, brown earths or rendzinas. Pelisek (1940 b) reports contents of Ba and Sr, these being generally greatest in soils derived from carbonate rocks and being leached from the upper layers of podzols.

Cr, Zn, Ni and Co were discussed together (Pelisek, 1941). Cr appeared to be leached in the podzolization process. The highest contents were in soils on serpentine and andesite. Zn contents were highest in the B horizon of podzols whilst in other soil types it was also observed. Soils on amphibolite schist, diabase, diorite and cretaceous clay contained more Zn than those on gneiss, phyllite, granite, pegmatite and sandstone. Co and Ni were observed only in a few soils, with higher contents in the lower layers. Pelisek (1942) discussed the Sn content of granitic soils and reported an accumulation of Sn in the surface layers presumably because of biological action. The parent granite in one instance contained 0.01% SnO_2 whilst 0.05-0.1% was found in the 5-15 cm. horizon. A general account of the trace elements in the soils of the region has been given by Novak and Pelisek (1940). Bertrand has studied the content of alkalis, gallium and molybdenum in French soils in a series of papers (Bertrand, 1940, 1941, 1943, 1947 a, b; Bertrand and Bertrand, 1946).

Sedletsky and Ivanov (1941) found accumulation of Cu in the upper part of the A horizon of podzols, similar to that found by Pelisek for Sn and in extension of the results of Goldschmidt (1937) who found accumulations of many other trace constituents in the litter and humus layers of forest soils. Data are given by Goldschmidt for the concentration of B, Mn, Ni, Ge, As, Ag and Au, whilst other elements concentrated include

Be, Co, Zn, Cd, Sn, Pb and Tl. Sedletsky and Ivanov (1941) found, in Russian soils, less than 3 p.p.m. of Cu in a highly podzolized sand, 32 p.p.m. in a peaty podzol, 60 p.p.m. in a chernozem and 140 p.p.m. in a red earth.

Davidson and Mitchell (1940 a, b) have given data for Cr and Co for a few Scottish soils by a quantitative cathode layer arc method, comparing the results with colorimetric determinations. Co contents of 1-150 p.p.m. and Cr from 150 to 3000 p.p.m. are recorded, but many soils have lower Cr contents. Nichols and Rogers (1944) have made a similar comparison for Mo in organic soils and plants, finding up to 26 p.p.m. of Mo in the ash of peats.

Rao (1937 a, b, c) has studied the trace element content of soils, and in an investigation of fertile and infertile sugarcane soils has suggested the possible influence of Zn, Mn and Ti.

The total rare earth content of most Russian soils has been given as about 0.02% by Borneman-Starynkevich, Borovik and Borovsky (1941).

Konishi and Tsuge (1936 a) have dealt with the determination of trace elements in Japanese soils, whilst Oertel (1937, 1944 a) has discussed generally the methods of spectrographic determination of trace elements in soils.

The trace constituents present in any soil are not present in completely random amounts, but, particularly where the soil is derived from an igneous rock, it is often possible, from a knowledge of the geological parent material, to anticipate which trace constituents are likely to be present in high and which in low contents. This knowledge has been derived from analysis of rocks and minerals, much of which has been carried out spectrographically. Reference has already been made to the work of Goldschmidt and his collaborators in Göttingen during the years 1930-1935 when the foundations of much of the geochemical spectrographic work were laid, and the cathode layer arc technique worked out. The geochemical applications of this work have been discussed by Goldschmidt (1937, 1938) whilst the current position as far as soils are concerned has also been summarized (Goldschmidt, 1945). Wager and Mitchell (1943) and Nockolds and Mitchell (1948) have given spectrographic results for trace constituents in series of igneous rocks varying from basic to acidic in character, and have given further confirmation of the geochemical principles governing the distribution of trace constituents in igneous rocks. Nockolds and Mitchell have also analysed constituent minerals of the rocks, indicating in which the trace constituents are found. Results for over 200 rocks from the Dutch East Indies have been given by Tongeren (1938), from which the trend of many trace constituent contents throughout igneous and sedimentary rocks can be observed. Results of a similar nature are given by Bray (1942 a, b), Sahama (1945 a, b), Rankama (1946) and P. H. Lundegårdh (1946 a), to cite only the more comprehensive communications based on spectrographic analyses, whilst the non-spectrographic contributions of Sandell and Goldich (1943) and Hutchinson (1943) in particular must be noted in this connexion.

The results of this work which are of particular significance for soil investigations may be summarized briefly. In igneous rocks the distribution of trace constituents is controlled in the main by the ionic radii of the elements concerned. Elements present in trace amounts in the magma from which the rocks are crystallizing are included in the crystal lattice of those minerals which contain a major constituent of equivalent ionic radius ($\pm 15\%$ difference is permissible), and are thus concentrated in those rocks which contain that particular mineral. In such typical ferro-magnesium minerals as olivines, pyroxenes, amphiboles and biotite micas Mg^{++}(0.78A) and Fe^{++}(0.83A), which are themselves mutually interchangeable, are replaced by such trace constituents as Li^{+}(0.78A), Ni^{++}(0.78A), Co^{++}(0.82A), Zn^{++}(0.83A), Mn^{++}(0.91A), Sc^{+++}(0.83A) and others of similar ionic radius. Where valency differences occur, the more highly charged ion tends to enter preferentially, whilst Ni with a slightly smaller radius than Co is found in earlier crystallizing rocks. As such ferromagnesium minerals are typical of the basic igneous rock suites, trace constituents such as Ni and Co occur in such rocks (peridotites, gabbros, diorites, etc.) in greater amounts than in the acid igneous types. On the other hand, trace constituents with larger ionic radii, such as Pb^{++}(1.32A), Sr^{++}(1.27A), Ba^{++}(1.43A) and Rb^{+}(1.49A) replace K^{+}(1.33A) in the potassium felspars and are typical of acid igneous rocks. It is impossible here to discuss the distribution of trace constituents in igneous rocks in more detail. It will be obvious, however, that, as our knowledge of such relationships increases, it will become more possible to anticipate the total trace element content of any soil derived from such rocks. The application of spectrographic methods to the determination of the total content of trace constituents in soils and the materials from which they are derived should lead eventually to a much clearer understanding of the factors which could possibly be involved in undiagnosed disorders of plants and animals. The problem is at present rather less clear where sedimentary and metamorphic rocks are concerned. The processes involved are those of dissolution and precipitation, hydrolysis and evaporation, oxidation and reduction, with the ionic potential of the ions concerned playing a major part in the redistribution of the trace constituents throughout the different strata. Thus we find that Ni and Mg, which are closely related in igneous rocks, are no longer associated, as is shown by the low Ni contents of dolomitic limestones.

Ahrens (1945 a) has analysed 34 South African clays for Ag (10), Ba (30), Be, Bi, Cb, Cd (1), Co (28), Cr (32), Cu (29), Ga (32), Ge, In, K (23), La, Li (15), Mn (33), Mo (2), Na (28), Ni (32), Pb (20), Pd (1), Pt, Sb, Se (17), Sn (13), Sr (28), Tl (14), V (31), W, Y (18), Zn (3) and Zr (28), the figure in brackets indicating the number of samples in which it was detected, if at all. Tl, Ga and Sc are discussed in some detail. Austin and Bassett (1943) record the presence of B, Sb and Be in some American ceramic clays in addition to the elements observed by Ahrens.

Bosazza (1940, 1941) has studied some South African fire clays, and Monfort (1942) 40 samples of plastic earths from Belgium, finding B, Cr, Li and perhaps Mn, but not confirming V which was reported by all the above workers with ceramic clays.

(ii) *Analysis of soil extracts*

The analysis of soil extracts can be divided roughly into the determination of alkalis, alkaline earths and manganese in exchangeable base or similar leachates by the Lundegårdh flame technique and the determination of trace constituents in evaporates or concentrates by arc methods.

Little purpose can be served here by dealing in detail with the first category, as the flame technique is merely a routine method of obtaining results similar to those obtainable by other methods, and their interpretation is scarcely relevant to the present work. Many of the results obtained have been for purely advisory purposes (Mitchell, 1939; Hamilton, 1941) principally for K, and it is necessary only to point out the advantage of having a reference plate carrying also data for Mg, Mn, Na and Sr should they be required. This advantage of a photographic method over the direct photometry technique should be noted. Examples of the results obtained from extracts of soils by the Lundegårdh method are those of Muir and Fraser (1940), Glentworth (1944) and Stewart (1941). The first two papers discuss the exchangeable cation contents in profiles of uncultivated and cultivated soils from areas in Aberdeenshire, where interesting zones of Ca accumulation in the lower layers are noted. Stewart deals with hydrochloric acid, acetic acid and ammonium acetate soluble Ca, Mg and K in soils on which grass sickness in horses has occurred, without finding any correlation between soil composition and the disease. Mitchell (1937) has pointed out the similarity in behaviour of Ca and Sr in the soil profile, in the course of an investigation of Ca, Sr, Mg, Mn, K and Na in a series of profiles. The flame method may occasionally disclose an excess of a trace constituent, for example the high contents of acetic acid and ammonium acetate soluble Ni and Cu in certain infertile areas of Aberdeenshire (Mitchell, 1945) where 50-80 p.p.m. of Ni are extracted by 2.5% acetic acid. Rodriguez (1943) has given results for solutions obtained by the electrodialysis of soils. Ballard and Mills (1942) describe the determination of potassium in sodium acetate soil extracts, using the condensed spark.

The use of the arc method for trace constituents in soil extracts must generally be combined with one of the concentration methods already discussed in order to get rid of the relatively large amounts of certain elements, particularly Ca, which are extracted. In a series of papers results of this procedure for the determination of Co in acetic acid extracts of soils associated with pining in sheep have been given (Stewart, Mitchell and Stewart, 1941, 1942; Stewart, Mitchell, Stewart and Young, 1946). Some data for other trace constituents such as Ni, V, Cr, Mo, Ti, Sn, Pb and Zn extracted from soils and concentrated in the same manner by mixed organic reagents (Mitchell and Scott, 1947) have been given (Mitchell, 1946), but

interpretation of such results is not yet clear. It is clear, however, that extraction media will have to be carefully chosen, as molybdenum solubility, for instance, increases in neutral or alkaline media whilst cobalt and nickel are more soluble in acid conditions. As already pointed out, the interpretation of results of analyses of soil extracts will remain difficult until an adequate amount of data on normal contents is available.

The precise determination of soil colour by means of the spectrograph has been studied by Ramamurthy and Viswa Nath (1944). From reflectance data, it was found that soil colour could be investigated as a continuous variable, determined, in Indian soils, by the inorganic rather than the organic constituents.

b. Plant Materials

There have been several surveys of the range of contents found for different species of plant on one soil or for the same species on different soils. Thus Breckpot (1936 a) found K, Na, Rb, Mg, Ca, Ba, Cu, Pb, Ag, Tl, Mo, Sn, Fe, Mn, Ni, Al, B, Si, P and traces of Sr, Co and Ti in sugar beet, using either the total ash or an H_2S concentrate from an HNO_3-H_2SO_4 extraction. Li was observed in tobacco, potatoes and carrots but not in tea. In an examination of hays and grain mixtures Hodgkiss and Errington (1941) found Cu, Mn, Zn, Ba, Sr, Li, Sn, Mo, Al, Pb, Cr, Ni, Co, V, Ti and B in all six samples inspected. Konishi and Tsuge (1936 b) investigated the contents of nodules of leguminous crops, finding small quantities of Li, Sr, Cr, Zn, Ni, Co, Cu, V, Mo, Pb, B and traces of Ba, Mn and Ti. Mitchell (1944) reports contents in pasture herbages from north-east Scotland of Ba 10-30, Co 0.03-0.6, Cr 0.1-0.5, Cu 2-14, Fe 50-150, Li 0.05-0.15, Mn 20-300, Mo 0.3-6.0, Ni 0.5-4.0, Rb 5-15, Sr 4-20, Ti 2-15, V 0.3-0.7, and Zn 5-40 p.p.m. The contents of Fe, Mn, Cu, Ca, K and Mg in brome grass were determined by Nelson, Hamm and Tsiang (1943), whilst Rusoff, Rogers and Gaddum (1937) found, in Florida wire grasses, Al, Ba, B, Cu, Pb, Mn, Sr, Ti and Zn in all, Cr, Mo, Ag and Ni in some, and Sb, As, Be, Bi, Cd, Co, La, Th, Sn, V, Y and Zr in none. Such results depend on the sensitivity of the method employed, and a negative report for an element is never absolute. They are representative of the information which can be obtained by spectrographic methods, indicating those elements which can be observed spectrographically in normal plant materials. The values quoted by Mitchell for Fe of 50 to 150 p.p.m. are much lower than many quoted in the literature. These are the values obtained from pasture herbage as nearly as possible uncontaminated with soil, during the summer growth period, and higher values must be suspect, owing to the difficulty of getting a clean sample. With high Fe contents, due to soil contamination, will be associated high Co, Ni, Ti, Cr and possibly V and other elements, in view of the much higher total contents of these constituents in soils than in plant materials. Experience has shown the great difficulty of obtaining a clean herbage sample even by careful cutting from a field in which stock are grazing.

Plucking of grass samples has proved to be quite unsatisfactory. The problem of sampling pasture herbage is not yet solved, as a fenced off portion is probably not quite representative and washing of cut samples has several objectionable features. Most other plant materials are easier to obtain in an uncontaminated condition, although difficulty may be experienced with hairy leaves such as those of turnips. In a series of papers Azcona and his co-workers have recorded the trace constituents present in various types of Spanish plants and plant materials (Ruiz, Gerpe and Azcona, 1944; Azcona, Ruiz and Guelbenzu, 1945; Guelbenzu, Azcona and Ruiz, 1946 ; Ruiz, Guelbenzu and Azcona, 1946 ; Azcona, Ruiz and Guelbenzu, 1946, a, b).

Materials similar in nature to plants have been studied by numerous workers. In calcareous algae, Lagrange and Tchakirian (1939) found Ag, As, Cu, Ge, Be, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, W and Zn. High Ag contents have been observed by Ramage (1930) in certain fungi. Curran, Brunstetter and Myers (1943) have analysed vegetative cells and spores of 12 aerobic species of bacteria for K, Ca, P, Mg, Fe, Al, Cu, Mn and B. Richards and Troutman (1940) have studied the metallic nutrient requirements of yeast. Wilson and Fieldes (1942 a) have given some results for seaweed.

Rao (1938, 1940) has studied the Zn, Mn and Mo contents of various plants, reporting high Mo contents for peas, in line with the general findings for legumes. Zn contents varied from 20-60 p.p.m. except for polished rice which contained only 2 p.p.m. Rao notes also that cereals are high in Sr and Rb, whilst a spinach sample showed a high Mg content. Sibaiya and Rao (1941) have given results for Ca, Mg, Cu, Mn, Sr and Si in various fruits. Ambrosis (1942) reports that the ashes of 14 different fruits and vegetables contained Al, Mn, Cu, Mg, Ba, Fe, K, Zn, Si, P, Na, Sr and Ni.

Employing the technique of Brunstetter, Myers, Wilkins and Hein (1939) and Brunstetter and Myers (1941), Magoon, Myers, Dix and Brunstetter (1938), Brunstetter, Myers, Dix and Magoon (1939), and Myers, Brunstetter, Dix and Magoon (1939) have studied the content of Mg, Mn, Ca, Al, Cu, Fe, K and P in young grape leaves of different varieties grown on the same soil or of differently treated vines of the same varieties. Quite large varietal differences were observed for all the elements determined. When such varietal differences are considered in conjunction with such data as those of Goodall (1943, 1945 a, b) for Ca, Fe, Mg, Mn and K for apical, middle and basal leaves of different shoot types, and with the effects of seasonal variation of leaf content, the difficulties of the interpretation of leaf analysis become obvious. It is this problem that Lundegårdh (1938 b, 1941) has attempted to solve by the use of a " triple analysis " of plant material, soil extract and subsoil extract, paying attention not only to the actual contents but to molecular ratios, as he emphasizes that optimum yield is dependent not only on content but on the balance of the nutrients present, or on " ion-antagonism." A later monograph (Lundegårdh, 1945)

deals more specifically with leaf analysis alone. Burström (1934) studied the antagonistic behaviour of the various ions taken up by oats from culture solutions, attention being paid to the movement of ions in the plant and their effects on the growth of the different organs. Speed of ion uptake by the root was found to depend more on the rate of movement into the upper plant than on concentration in the root. Results showed that K reduced the uptake of Ca, Mg and Na, Ca that of K, Na, Mg and Mn, NH_3 that of Ca, and Mn that of K and Ca. Only for Na-Ca was no antagonistic effect noted. Marshall (1944), also using the Lundegårdh method, in a study of the exchangeable bases of two Missouri soils in relation to the composition of four pasture species, concluded that, with different treatments, the total uptake of cations by the plant, per 100 g. of dry matter, in equivalents was relatively constant. Giesecke, Rathje and Krummel (1938) have determined K in plant ashes in the application of the Neubauer method of determination of the K status of the soil, whilst numerous other workers who employed the direct photometry technique for this purpose are cited on p. 105.

Kent (1942) has discussed the occurrence of Pb, Sn and Ag in wheat and its milling products, finding approximately 1 p.p.m. of Pb and Sn and half that amount of Ag in the whole wheat grain, with variations of up to ten fold over different parts of the grain. Kent and McCance (1941 a, b) have dealt with the application of spectrographic methods to the analysis of human food and excretion, covering the elements Ag, Au, Li, B, V, Co, Ni, Sn and Mn. This subject has also been investigated by Scoular (1938, 1939 a, b) and Brody and Ewing (1945).

Tate and Whalley (1940) in an investigation of tobacco ash by flame and arc methods, found that there was a high probability of being able successfully to identify the source of any tobacco from an analysis of the ash. McHargue and Hodge (1942) identified some 30 elements in tobacco.

A technique for the analysis of potato tracheal fluid, which contained B 0.01, Mg 0.1, Mn 0.01, Ca 0.01 and Cu 0.02 p.p.m. as well as Si, Al and Fe has been described by Hamm, Harvey and Miller (1941), whilst Moose (1938) gave chemical and spectrographic analyses of phloem exudate and parenchyma sap from several species of plant. Hibbard (1941) investigated the distribution and mobility of Ca, Mg, K, Fe, P and Mn in the tissues of plants, analysing sap and different extracts of leaves from various species of plants. Ether, acetone and water soluble extractions were studied.

Borovick-Romanova has investigated the content of alkali and alkaline earth metals in plants. The contents of Rb in land, marsh, fresh water and sea plants and in the media in which they grew have been determined (Borovick-Romanova, 1944 a, b, c) by flame and arc methods. Plants of all types contained about 1 p.p.m. of Rb on the fresh weight, although the contents of the media varied considerably, sea water being 50 times richer than river water. The Rb/K ratio is, on the other hand, much greater in land plants (0.002) than in sea algae (0.0004). The ratios in

soils (0.003) and sea water (0.0005) vary in a like manner. Borovick-Romanova (1939 a, b) has determined the Ba content of plants and marine organisms, whilst Borovick and Borovick-Romanova (1937 b) determined Sr in marine plants and animals. Bodunkov (1939) determined Li in plants, as did Kent (1940) for plants grown in soils and culture media to which Li had been added. Borovick, Bergman and Borovick-Romanova (1943) reported the trace elements present in kok-saghyz. Vanselow (1945) has studied the trace element content of normal, manganese deficient and manganese treated walnut trees.

Dingwall, McKibbin and Beans (1934) reported the presence of Mo in plants from certain areas of Quebec whilst Dingwall and Beans (1934) dealt with Cr. Keiller (1939) suggests that tea bushes affected with "witches broom" contain more Cr than unaffected plants. Rankama (1940) indicates the possibility of using plant analysis in geological mapping and prospecting, illustrating the increased content of Ni in the ash of plants in the neighbourhood of Ni deposits.

The content of rare earths in plants has been investigated by Scribner (1939) by the analysis of chemical concentrates. In hickory, Ce, La, Y, Pr, Nd, and less Sm, Eu, Gd, Yb, Dy and Er were found. Sweetleaf contained Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er and Yb, and birch leaf Sc, Y, La and Ce. Ho, Tm and Lu were not observed in any sample. Borneman-Starynkevich, Borovik and Borovskii (1941) found a total content in the ash of the whole plant of 3×10^{-3} to 2×10^{-4} with 0 to 5×10^{-3} in the green parts. The method of chemical separation depended on the isomorphism of the rare earths with Ca and was tested with Eu, which is probably the most favourable element for this method. Accumulation of rare earths was found in lupins, beet and maple leaves.

Carrigan and Rogers (1940), reporting the relationship of the content of fruit tissues (oranges) with the soils on which they have grown, found Al, B, Cu and Zn in all soils and plant tissues examined; Mn, Sr and Ba in all except two soils, in which they must have been present in amounts below the level of spectrographic detection by the method employed. Cr and Ni were observed irregularly in both soils and plants. Pb, Mo and Ag were detected in some plants, but never in soils, whilst Ti and Zr were observed in soils, but seldom if ever in plants. Gaddum, Camp and Reuther (1936), in a study of the composition of plant and soil for normal and physiologically diseased horticultural crops, found some correlation between foliage condition and Zn content in bronzing of tung trees and frenching of citrus. Although Tl produces symptoms similar to those of frenching of tobacco it seems unlikely from the spectrographic work of Shear and Ussery (1940) that Tl (or Ga) is responsible (see also Spencer and Lavin, 1939). Rankama and Sahama (1945) have challenged the results obtained by Turunen (1945) for plant ashes (*Erica*) because a comparison standard in a silica base was employed.

Mitchell (1944, 1945, 1946) has given some results for the relative uptakes of different trace constituents by different pasture species, with particular reference to Co and Ni. The effect of the relative amounts of clovers and grasses in mixed herbage is shown to be the important factor in the content of many trace constituents, and is possibly responsible for much of the variation in content at different times of sampling. The effect of soil acidity on the uptake of trace constituents by plants is also of importance. Liming can bring about reduced uptake of acid available constituents such as Co and Ni, whereas the uptake of Mo is increased. Table 6 indicates the type of information now being obtained at the Macaulay Institute.

TABLE 6

Typical Results Obtained Spectrographically at the Macaulay Institute for Plant Material by the Cathode Layer Arc Method : as parts per million Oven-dry Matter.

	Co	Ni	Mo	Pb	Sn	Zn	Ti
Mixed pasture herbage (a)	0.08	0.55	2.5	2.4	—	40	15.0
Mixed pasture herbage (b)	0.14	3.1	0.82	1.6	0.4	56	1.4
Red clover from (b) ...	0.30	6.8	0.74	1.8	0.4	103	1.6
Hill grazing (c)	0.08	0.64	0.25	6.5	0.3	32	16.0
Scirpus from (c)	0.06	1.08	0.44	1.3	0.3	38	2.3
Calluna from (c)	0.20	2.6	0.20	0.9	1.1	21	38.0

	V	Cr	Fe	Ba	Sr	Cu	
Mixed pasture herbage (a)	0.49	0.55	110	49	30	13.5	—
Mixed pasture herbage (b)	0.06	0.10	56	108	37	4.6	—
Red clover from (b) ...	0.10	0.11	98	220	137	12.5	—
Hill grazing (c)	0.50	0.25	122	9	11	8.0	—
Scirpus from (c)	0.10	0.20	103	11	5	6.4	—
Calluna from (c)	1.08	0.49	242	4	7	8.0	—

c. FERTILIZERS

Spectrographic analyses of fertilizers for trace constituents have been made almost exclusively by arc methods. Young (1935) examined chemically and spectrographically 53 samples from 13 sources and reported the following ranges—As 0-0.12%, B 0-0.7%, Ba 0-0.03%, Br 0-0.2%, Cr 0-0.5%, Cu 0-0.008%, I 0-0.0035%, Pb 0-0.2%, Mn 0-0.16%, Sr 0-0.2%, Ti 0-0.14% and V 0-0.24%. He discussed the possibility of adding useful elements during manufacturing processes and noted that the more unusual constituents were to be found in phosphatic and organic fertilizers, whilst natural potash salts and synthetic products are rather deficient in trace constituents. Gaddum and Rogers (1936), studying 18 trace elements in

64 fertilizers, found considerable variability from lot to lot. Ba, Sr, Cu, Mn, Cr and B were present in most samples, Bi, As, Sb, Cd, Sn and Ag were found in some, whilst Ti, Ni, Co, V, Pb and Zn were only occasionally detected. The greatest variety and largest quantities occurred in phosphatic materials, hardwood ashes and insoluble inorganic nitrogen sources whilst sources of K and inorganic N had least variety and small quantities. Breckpot (1935 c) found K, Mg, B, Ca, Sr, Li, Rb, Ba, Zn, Mn, Fe, Al, Cr, Ti, V, Ni, Pb, Cu, Mo, Sn, Ag, Si and P in Chilean nitrate of soda, but the total content of the twelve chief impurities did not exceed 3 p.p.m. and in some instances only 0.01 p.p.m. was found. Ballard (1938 b) found Ca, Mg, Fe, Cu, Zn, Al, Si, Na and Pb in by-product $(NH_4)_2SO_4$ and the same elements, except for Cu, Zn and Al, in a synthetic product from Canada. KNO_3 contained Ca, Mg, Fe, Al, Na, Sr and Ba whilst KCl had only Ca, Mg, Cu and Na detectable by direct analysis. Rock phosphates showed Mn, Mg, Cu, Zn, Ni, Ti, Pb, Cr, Sr, Ba and V whilst the same elements appeared in the derived superphosphates. A New Jersey " Ammo-phos " contained Ca, Mg, Fe, Mn, B, Cu, Al, Ni, Si, Na, Ti, Pb, Cr, Sr, V and Mo.

Melvin and O'Connor (1940, 1941) and O'Connor (1941) have given a method for Cu, Mn, B and Zn in mixed fertilizers using a direct current arc in preference to an alternating current arc with such samples, which proved to be rather homogeneous. They found CuO between 0.0007 and 0.01%, MnO 0.004-0.3, B_2O_3 0.006-0.5 and ZnO 0.003-0.25% for various N : P: K compound fertilizers from numerous sources over a ten year period. Allison and Whitehead (1943), examining such organic fertilizers as castor pomace, peanut meal, soybean meal, and cottonseed meal found Sr, Ba, Mn, Ni, Cu, B, Zn, Fe and Al in all, V, Cr, Mo and Ti in most and Sn, Pb and Y in some.

A dipping spark technique, modified from that of Lundegårdh (1934) has been employed by Bartelt (1938) for the quantitative determination of various trace constituents in solutions of compound fertilizers. Data are given for Mg, Sr, Mn, Fe, Cu, V, Cr and Ti in various N : P : K manures, and other proprietary fertilizers. Contents of Mn up to 50 p.p.m., Al up to 1000, Fe up to 1000, Cu up to 100, V up to 100, Cr up to 100 and traces only of Ti are reported. Sr rose to 1000 in lime rich fertilizers and Mg to 1% in a Norwegian dolomite saltpetre.

d. Water

There have been numerous analyses of various types of waters carried out spectrographically, both for general characterization of the trace constituents present and specific determinations of certain elements. Braidech and Emery (1935) report finding Al, Ba, B, Cu, Cr, F, Pb, Ni, Mn, K, Na, Ag, Sr and Zn in various water supplies in the United States. Charola (1939) found Na, Ca, Ba, Mg, Al, Si, Mn, Mo, Fe, Cu and K in an Argentine water supply. Kehoe, Cholak and Largent (1944) found Pb, Cu, Zn and As to be well below the U.S. limits in all waters examined, but the combined

Mn+Fe value was occasionally exceeded, this being ascribed to piping conditions. F was greater than 1 p.p.m. only where dental fluorosis was known. Sn, Hg and As were present in only a few samples. Ag was either absent or less than 0.0005 p.p.m. Pfeilsticker (1936) found Na, K, Si, Al, Fe, Cr, Mn, Pb, Zn and B in river waters in Germany.

Amongst analyses of mineral and mine waters and thermal springs, it is possible to refer only to a few of the more important. Schleicher and Kaiser (1936) found Hg, Ag, Pb, Sn, Bi, Sb, As, Cu, Te, Cd, Ga, W, Tl, Ni, Co, Zn, Mo, Al, Fe, Cr and Mn in a mine water after electrolytic concentration. Strock (1941 a) reported Zr, Sn, Be, Ti, V, Mn and Ni in Saratoga mineral waters. Intonti (1939) detected the presence, in Fonte di Fuiggi waters, of Ca, Mg, Si, K, Na, Mn, Cu, P, Fe, Cr and Ba, but did not observe Zn, V, Sn, B, Al, Rb, Ag, Pt or Pb. Analyses of mineral waters for alkali metals are reported by Jansen and Heyes (1932), Gazzi (1934, 1939), Bossuet (1934, 1935) and Lindtrop and Tolmachev (1936).

Novokhatski and Kalinin (1939 a, b, 1940 a, b, c) in a series of papers reported B, Fe, Al, Li, Sr, Mn, Mo, Cu, Pb, Zn and Ni in various mineral waters and thermal springs. Kuroda (1939 a, b, c) found 0.03 p.p.m. Ge, 0.04-0.08 p.p.m. Be, 0-0.25 p.p.m. V, 0-0.07 p.p.m. Cr and 0.0004-0.016 p.p.m. Mo in Japanese thermal springs. Forjaz (1933) suggests that the presence of Ge in a spring water is indication of a deep source. Rubies and d'Argent (1931) and Rubies and Bargués (1935) have also given analyses of medicinal springs. A paper by Azcona (1947) is apparently the first of a series dealing with Spanish medicinal waters.

e. Animal Tissues and Other Biological Materials

The migration of trace and major constituents from the rock through the soil to the plant can be followed a stage further into the animal. As already pointed out, certain disorders of stock are caused by abnormal trace constituent contents in the diet. This subject is so wide that only a few typical references can be given, especially when it is realized that medical work is also relevant. Unpublished spectrographic results obtained at the Macaulay Institute, in collaboration with the Animal Diseases Research Association, have confirmed the low Co content of organs, particularly the liver, in sheep suffering from Co deficiency.

The alkalis and alkaline earths in blood have been studied by numerous workers including Jansen, Heyes and Richter (1934 a) and Norinder (1938, 1939, 1942) using the Lundegårdh technique, Lamb (1941) and Zimmer (1939) for Mg, and Steadman (1941) for Na. Goldman and Armstrong (1936) have determined various elements, including Hg, by an arc method. Contents of Pb in blood have been reported by many workers.

Thomson and Lee (1937) have applied a spark method with a jet feed for the determination of Na, K, Ca and Mg in biological fluids. De (1935) found Na, Ca, Mg, P, K, Cu, Fe, Al, B, Mn, Pb, Ti and V in all the milks (human, cow, goat, buffalo) which he examined, but failed to detect Ba, Co,

Ni and Sn in any, whilst Cr, Li, Rb, Sr, Al and Si were doubtful. Co has been determined in sheep's milk by the concentration method in use at the Macaulay Institute.

Drea (1935) analysed hen eggs and chick tissues for Al, Ba, B, Cr, Cu, F, Fe, Pb, Mn, Mo, Rb, Si, Ag, Sr, Ti, V and Zn. All these elements except Rb and Zn were detected in the water, and all but F and Ag in the rations, consumed by the poultry. Ruthardt (1934) was able to carry out the determination of Ag, Au, Cu, Fe, Hg, Mn and Pb in a single spectrogram from a portion of tissue. The contents of trace constituents (Mn, Pb, Sn, Al, Cu, Ag) in biological materials are also reported by Kehoe, Cholak and Story (1940 a, b). McHargue and Hodge (1942) observed some 25 elements in bones of horses. Press and Fearon (1939) have worked with glandular tissues.

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APPENDIX I

TABLE OF $\log (i_o/i)$ FOR $i_o = 50$

i	0	1	2	3	4	5	6	7	8	9
0.	∞	2·699	2·398	2·222	2·097	2·000	1·921	1·854	1·796	1·745
1.	1·699	1·659	1·620	1·585	1·553	1·523	1·495	1·469	1·444	1·420
2.	1·398	1·377	1·357	1.337	1·319	1·301	1·284	1·268	1·251	1·236
3.	1·222	1·208	1·194	1·181	1·168	1·155	1·143	1·131	1·119	1·108
4.	1·097	1·086	1·076	1·066	1·056	1·046	1·036	1·027	1·018	1·009
5.	1·000	0·991	0·982	0·975	0·967	0·959	0·951	0·943	0·936	0·928
6.	0·921	0·914	0·907	0·900	0·890	0·886	0·880	0·873	0·867	0·860
7.	0·854	0·848	0·842	0·836	0·830	0·824	0·818	0·813	0·807	0·801
8.	0·796	0·791	0·785	0·780	0·775	0·770	0·765	0·760	0·755	0·750
9.	0·745	0·740	0·735	0·731	0·726	0·721	0·717	0·713	0·708	0·703
10.	0·699	0·695	0·690	0·686	0·682	0·678	0·674	0·670	0·666	0·662
11.	0·659	0·654	0·650	0·646	0·642	0·638	0·635	0·631	0·627	0·624
12.	0·620	0·616	0·613	0·609	0·606	0·602	0·599	0·595	0·592	0·588
13.	0·585	0·582	0·579	0·575	0·572	0·569	0·566	0·562	0·559	0·556
14.	0·553	0·550	0·547	0·544	0·541	0·538	0·535	0·532	0·529	0·526
15.	0·523	0·520	0·517	0·514	0·512	0·509	0·506	0·503	0·500	0·498
16.	0·495	0·492	0·490	0·487	0·484	0·482	0·479	0·476	0·474	0·471
17.	0·469	0·466	0·463	0·461	0·459	0·456	0·454	0·451	0·449	0·447
18.	0·444	0·441	0·439	0·437	0·434	0·432	0·430	0·428	0·424	0·423
19.	0·420	0·418	0·416	0·413	0·411	0·409	0·407	0·405	0·403	0·400
20.	0·398	0·396	0·394	0·392	0·389	0·387	0·385	0·383	0·381	0·379
21.	0·377	0·375	0·373	0·371	0·369	0·367	0·365	0·363	0·361	0·359
22.	0·357	0·355	0·353	0·351	0·349	0·347	0·345	0·343	0·341	0·339
23.	0·337	0·335	0·334	0·332	0·330	0·328	0·326	0·324	0·322	0·321
24.	0·319	0·317	0·315	0·313	0·312	0·310	0·308	0·306	0·305	0·303
25.	0·301	0·299	0·298	0·296	0·294	0·293	0·291	0·289	0·287	0·286
26.	0·284	0·282	0·281	0·279	0·277	0·276	0·274	0·273	0·271	0·269
27.	0·268	0·266	0·264	0·263	0·261	0·260	0·258	0·257	0·255	0·253
28.	0·251	0·250	0·249	0·247	0·246	0·244	0·243	0·241	0·240	0·238
29.	0·236	0·235	0·234	0·232	0·231	0·229	0·228	0·226	0·225	0·223
30.	0·222	0·220	0·219	0·218	0·216	0·215	0·213	0·212	0·210	0·209
31.	0·208	0·206	0·205	0·204	0·202	0·201	0·199	0·198	0·197	0·196
32.	0·194	0·193	0·191	0·190	0·189	0·187	0·186	0·185	0·183	0·182
33.	0·181	0·179	0·178	0·177	0·175	0·174	0·173	0·171	0·170	0·169
34.	0·168	0·166	0·165	0·164	0·162	0·161	0·160	0·159	0·157	0·156
35.	0·155	0·154	0·153	0·151	0·150	0·149	0·148	0·146	0·145	0·144
36.	0·143	0·142	0·140	0·139	0·138	0·137	0·136	0·134	0·133	0·132
37.	0·131	0·130	0·129	0·127	0·126	0·125	0·124	0·123	0·122	0·120
38.	0·119	0·118	0·117	0·115	0·114	0·113	0·112	0·111	0·110	0·109
39.	0·108	0·107	0·106	0·105	0·103	0·102	0·101	0·100	0·099	0·098
40.	0·097	0·096	0·095	0·094	0·093	0·091	0·090	0·089	0·088	0·087
41.	0·086	0·085	0·084	0·083	0·082	0·081	0·080	0·079	0·078	0·077
42.	0·076	0·075	0·074	0·073	0·072	0·071	0·070	0·069	0·068	0·067
43.	0·066	0·064	0·063	0·062	0·061	0·060	0·059	0·058	0·057	0·057
44.	0·056	0·055	0·054	0·053	0·052	0·051	0·050	0·049	0·048	0·047
45.	0·046	0·045	0·044	0·043	0·042	0·041	0·040	0·039	0·038	0·037
46.	0·036	0·035	0·034	0·033	0·032	0·031	0·031	0·030	0·029	0·028
47.	0·027	0·026	0·025	0·024	0·023	0·022	0·021	0·020	0·020	0·019
48.	0·018	0·017	0·016	0·015	0·014	0·013	0·012	0·011	0·011	0·010
49.	0·009	0·008	0·007	0·006	0·005	0·004	0·003	0·003	0·002	0·001

APPENDIX II

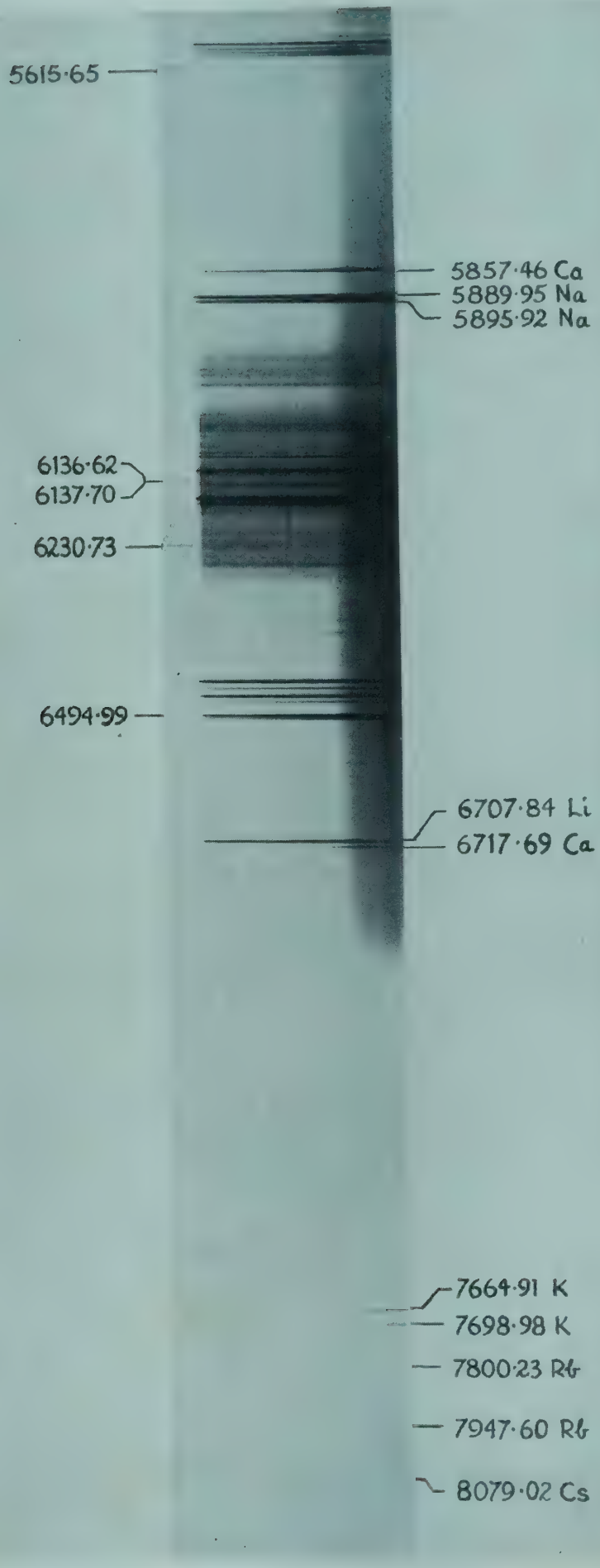
TABLE OF $(\delta - \gamma)$ FOR VALUES OF δ, WHERE γ IS THE SUBTRACTION LOGARITHM OF δ

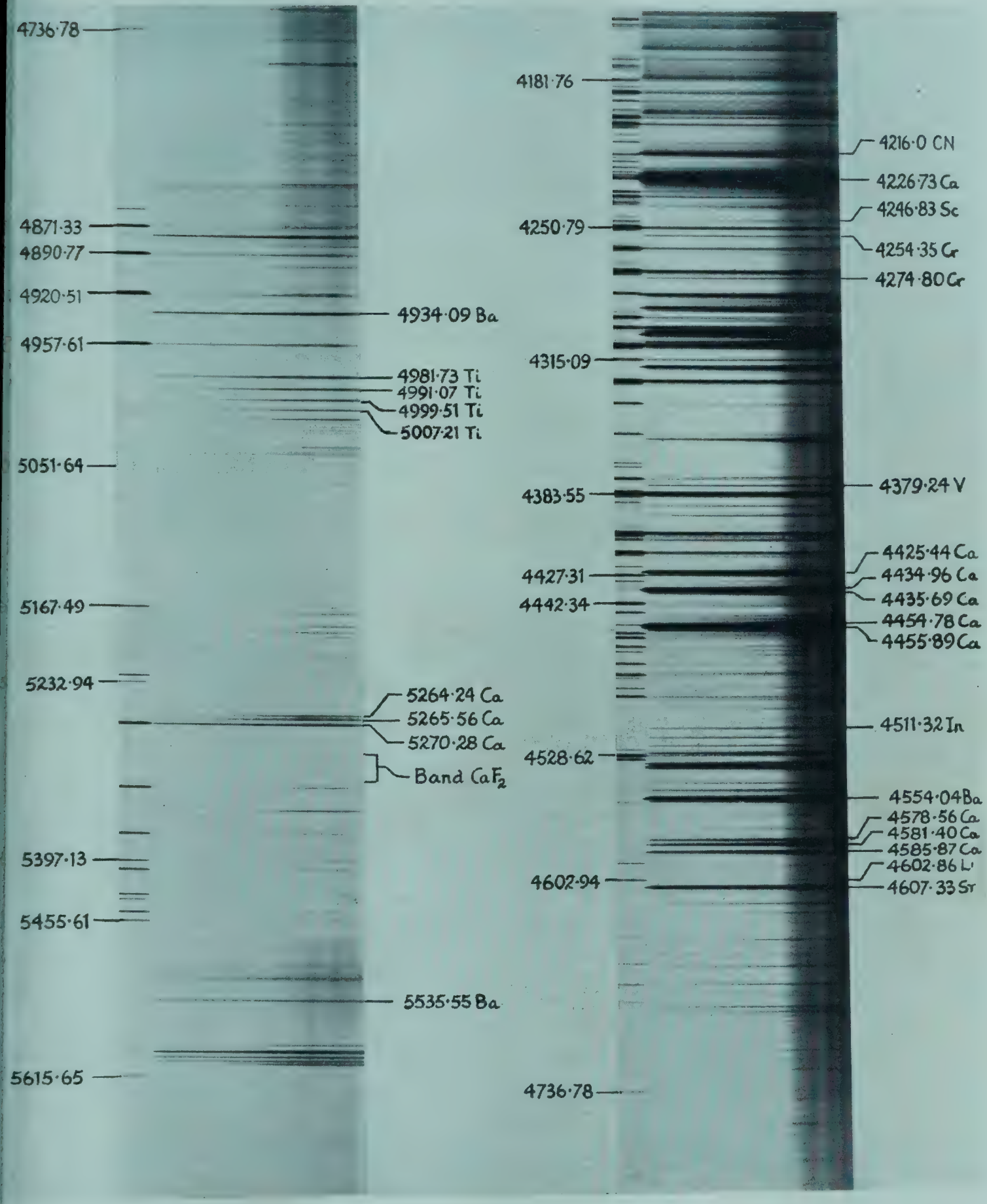
δ	0	1	2	3	4	5	6	7	8	9
0.00		$\bar{3}$·363	$\bar{3}$·664	$\bar{3}$·841	$\bar{3}$·966	$\bar{2}$·064	$\bar{2}$·143	$\bar{2}$·211	$\bar{2}$·269	$\bar{2}$·321
0.01	$\bar{2}$·367	$\bar{2}$·409	$\bar{2}$·447	$\bar{2}$·483	$\bar{2}$·513	$\bar{2}$·546	$\bar{2}$·574	$\bar{2}$·601	$\bar{2}$·627	$\bar{2}$·651
0.02	$\bar{2}$·673	$\bar{2}$·695	$\bar{2}$·716	$\bar{2}$·735	$\bar{2}$·754	$\bar{2}$·773	$\bar{2}$·790	$\bar{2}$·807	$\bar{2}$·823	$\bar{2}$·839
0.03	$\bar{2}$·854	$\bar{2}$·869	$\bar{2}$·883	$\bar{2}$·897	$\bar{2}$·911	$\bar{2}$·924	2·937	$\bar{2}$·949	$\bar{2}$·961	$\bar{2}$·973
0.04	$\bar{2}$·985	$\bar{2}$·996	$\bar{1}$·007	$\bar{1}$·017	$\bar{1}$·028	$\bar{1}$·038	$\bar{1}$·048	$\bar{1}$·058	$\bar{1}$·068	$\bar{1}$·077
0.05	$\bar{1}$·086	$\bar{1}$·096	$\bar{1}$·104	$\bar{1}$·113	$\bar{1}$·122	$\bar{1}$·130	$\bar{1}$·139	$\bar{1}$·147	$\bar{1}$·155	$\bar{1}$·163
0.06	$\bar{1}$·171	$\bar{1}$·178	$\bar{1}$·186	$\bar{1}$·193	$\bar{1}$·201	$\bar{1}$·208	$\bar{1}$·215	$\bar{1}$·222	$\bar{1}$·229	$\bar{1}$·236
0.07	$\bar{1}$·243	$\bar{1}$·250	$\bar{1}$·256	$\bar{1}$·263	$\bar{1}$·269	$\bar{1}$·275	$\bar{1}$·282	$\bar{1}$·288	$\bar{1}$·294	$\bar{1}$·300
0.08	$\bar{1}$·306	$\bar{1}$·312	$\bar{1}$·318	$\bar{1}$·323	$\bar{1}$·329	$\bar{1}$·335	$\bar{1}$·340	$\bar{1}$·346	$\bar{1}$·351	$\bar{1}$·357
0.09	$\bar{1}$·362	$\bar{1}$·368	$\bar{1}$·373	$\bar{1}$·378	$\bar{1}$·383	$\bar{1}$·388	$\bar{1}$·393	$\bar{1}$·398	$\bar{1}$·403	$\bar{1}$·408
0.10	$\bar{1}$·413	$\bar{1}$·418	$\bar{1}$·423	$\bar{1}$·429	$\bar{1}$·432	$\bar{1}$·437	$\bar{1}$·442	$\bar{1}$·446	$\bar{1}$·451	$\bar{1}$·455
0.11	$\bar{1}$·460	$\bar{1}$·464	$\bar{1}$·469	$\bar{1}$·473	$\bar{1}$·477	$\bar{1}$·482	$\bar{1}$·486	$\bar{1}$·490	$\bar{1}$·494	$\bar{1}$·499
0.12	$\bar{1}$·503	$\bar{1}$·507	$\bar{1}$·511	$\bar{1}$·515	$\bar{1}$·519	$\bar{1}$·523	$\bar{1}$·527	$\bar{1}$·531	$\bar{1}$·535	$\bar{1}$·539
0.13	$\bar{1}$·543	$\bar{1}$·547	$\bar{1}$·550	$\bar{1}$·554	$\bar{1}$·558	$\bar{1}$·562	$\bar{1}$·566	$\bar{1}$·569	$\bar{1}$·573	$\bar{1}$·577
0.14	$\bar{1}$·580	$\bar{1}$·584	$\bar{1}$·587	$\bar{1}$·591	$\bar{1}$·595	$\bar{1}$·598	$\bar{1}$·602	$\bar{1}$·605	$\bar{1}$·609	$\bar{1}$·612
0.15	$\bar{1}$·615	$\bar{1}$·619	$\bar{1}$·622	$\bar{1}$·625	$\bar{1}$·629	$\bar{1}$·632	$\bar{1}$·636	$\bar{1}$·639	$\bar{1}$·642	$\bar{1}$·646
0.16	$\bar{1}$·649	$\bar{1}$·652	$\bar{1}$·655	$\bar{1}$·658	$\bar{1}$·662	$\bar{1}$·665	$\bar{1}$·668	$\bar{1}$·671	$\bar{1}$·674	$\bar{1}$·677
0.17	$\bar{1}$·680	$\bar{1}$·684	$\bar{1}$·687	$\bar{1}$·690	$\bar{1}$·693	$\bar{1}$·696	$\bar{1}$·699	$\bar{1}$·702	$\bar{1}$·705	$\bar{1}$·708
0.18	$\bar{1}$·711	$\bar{1}$·714	$\bar{1}$·716	$\bar{1}$·719	$\bar{1}$·722	$\bar{1}$·725	$\bar{1}$·728	$\bar{1}$·731	$\bar{1}$·734	$\bar{1}$·737
0.19	$\bar{1}$·740	$\bar{1}$·742	$\bar{1}$·745	$\bar{1}$·748	$\bar{1}$·750	$\bar{1}$·753	$\bar{1}$·756	$\bar{1}$·759	$\bar{1}$·762	$\bar{1}$·764
0.20	$\bar{1}$·767	$\bar{1}$·770	$\bar{1}$·772	$\bar{1}$·775	$\bar{1}$·778	$\bar{1}$·781	$\bar{1}$·783	$\bar{1}$·786	$\bar{1}$·788	$\bar{1}$·791
0.21	$\bar{1}$·794	$\bar{1}$·796	$\bar{1}$·799	$\bar{1}$·801	$\bar{1}$·804	$\bar{1}$·807	$\bar{1}$·809	$\bar{1}$·812	$\bar{1}$·814	$\bar{1}$·817
0.22	$\bar{1}$·820	$\bar{1}$·822	$\bar{1}$·824	$\bar{1}$·827	$\bar{1}$·829	$\bar{1}$·832	$\bar{1}$·834	$\bar{1}$·837	$\bar{1}$·839	$\bar{1}$·842
0.23	$\bar{1}$·844	$\bar{1}$·847	$\bar{1}$·849	$\bar{1}$·851	$\bar{1}$·854	$\bar{1}$·856	$\bar{1}$·858	$\bar{1}$·861	$\bar{1}$·863	$\bar{1}$·866
0.24	$\bar{1}$·868	$\bar{1}$·870	$\bar{1}$·873	$\bar{1}$·875	$\bar{1}$·877	$\bar{1}$·880	$\bar{1}$·882	$\bar{1}$·884	$\bar{1}$·887	$\bar{1}$·889
0.25	$\bar{1}$·892	$\bar{1}$·894	$\bar{1}$·896	$\bar{1}$·898	$\bar{1}$·900	$\bar{1}$·902	$\bar{1}$·905	$\bar{1}$·907	$\bar{1}$·909	$\bar{1}$·911
0.26	$\bar{1}$·914	$\bar{1}$·916	$\bar{1}$·918	$\bar{1}$·920	$\bar{1}$·923	$\bar{1}$·925	$\bar{1}$·927	$\bar{1}$·929	$\bar{1}$·931	$\bar{1}$·933
0.27	$\bar{1}$·935	$\bar{1}$·938	$\bar{1}$·940	$\bar{1}$·942	$\bar{1}$·944	$\bar{1}$·946	$\bar{1}$·948	$\bar{1}$·951	$\bar{1}$·953	$\bar{1}$·955
0.28	$\bar{1}$·957	$\bar{1}$·959	$\bar{1}$·961	$\bar{1}$·963	$\bar{1}$·965	$\bar{1}$·967	$\bar{1}$·970	$\bar{1}$·972	$\bar{1}$·974	$\bar{1}$·976
0.29	$\bar{1}$·978	$\bar{1}$·980	$\bar{1}$·982	$\bar{1}$·983	$\bar{1}$·985	$\bar{1}$·987	$\bar{1}$·989	$\bar{1}$·992	$\bar{1}$·994	$\bar{1}$·996
0.30	$\bar{1}$·998	0·000	0·002	0·004	0·006	0·008	0·010	0·012	0·014	0·016
0.31	0·018	0·020	0·022	0·024	0·026	0·028	0·030	0·031	0·033	0·035
0.32	0·037	0·039	0·041	0·043	0·045	0·047	0·049	0·050	0·052	0·054
0.33	0·056	0·058	0·060	0·062	0·064	0·066	0·067	0·069	0·071	0·073
0.34	0·075	0·077	0·078	0·080	0·082	0·084	0·086	0·088	0·089	0·091
0.35	0·093	0·095	0·097	0·098	0·100	0·102	0·104	0·106	0·107	0·109
0.36	0·111	0·113	0·114	0·116	0·118	0·120	0·122	0·123	0·125	0·127
0.37	0·128	0·130	0·131	0·133	0·135	0·136	0·138	0·140	0·142	0·144
0.38	0·146	0·148	0·149	0·151	0·153	0·154	0·156	0·158	0·159	0·161
0.39	0·163	0·165	0·166	0·168	0·170	0·171	0·173	0·175	0·176	0·178
0.40	0·180	0·181	0·183	0·185	0·186	0·188	0·190	0·191	0·193	0·195
0.41	0·196	0·198	0·200	0·201	0·203	0·204	0·206	0·208	0·209	0·211
0.42	0·213	0·214	0·216	0·217	0·219	0·221	0·222	0·224	0·225	0·227
0.43	0·229	0·230	0·232	0·233	0·235	0·236	0·238	0·240	0·241	0·243
0.44	0·244	0·246	0·248	0·249	0·251	0·252	0·254	0·255	0·257	0·258
0.45	0·260	0·261	0·263	0·265	0·266	0·268	0·269	0·271	0·272	0·274
0.46	0·275	0·277	0·278	0·280	0·281	0·283	0·284	0·286	0·287	0·289
0.47	0·291	0·292	0·294	0·295	0·297	0·298	0·300	0·301	0·303	0·304
0.48	0·306	0·307	0·309	0·310	0·312	0·313	0·314	0·316	0·317	0·319
0.49	0·320	0·322	0·323	0·325	0·326	0·328	0·329	0·331	0·332	0·334
0.50	0·335	0·336	0·338	0·339	0·341	0·342	0·344	0·345	0·347	0·348
0.51	0·349	0·351	0·352	0·354	0·355	0·357	0·358	0·360	0·361	0·362
0.52	0·364	0·365	0·367	0·368	0·370	0·371	0·372	0·374	0·375	0·377
0.53	0·378	0·380	0·381	0·382	0·384	0·385	0·387	0·388	0·389	0·391
0.54	0·392	0·394	0·395	0·396	0·398	0·399	0·401	0·402	0·403	0·405
0.55	0·406	0·408	0·409	0·410	0·412	0·413	0·415	0·416	0·417	0·419

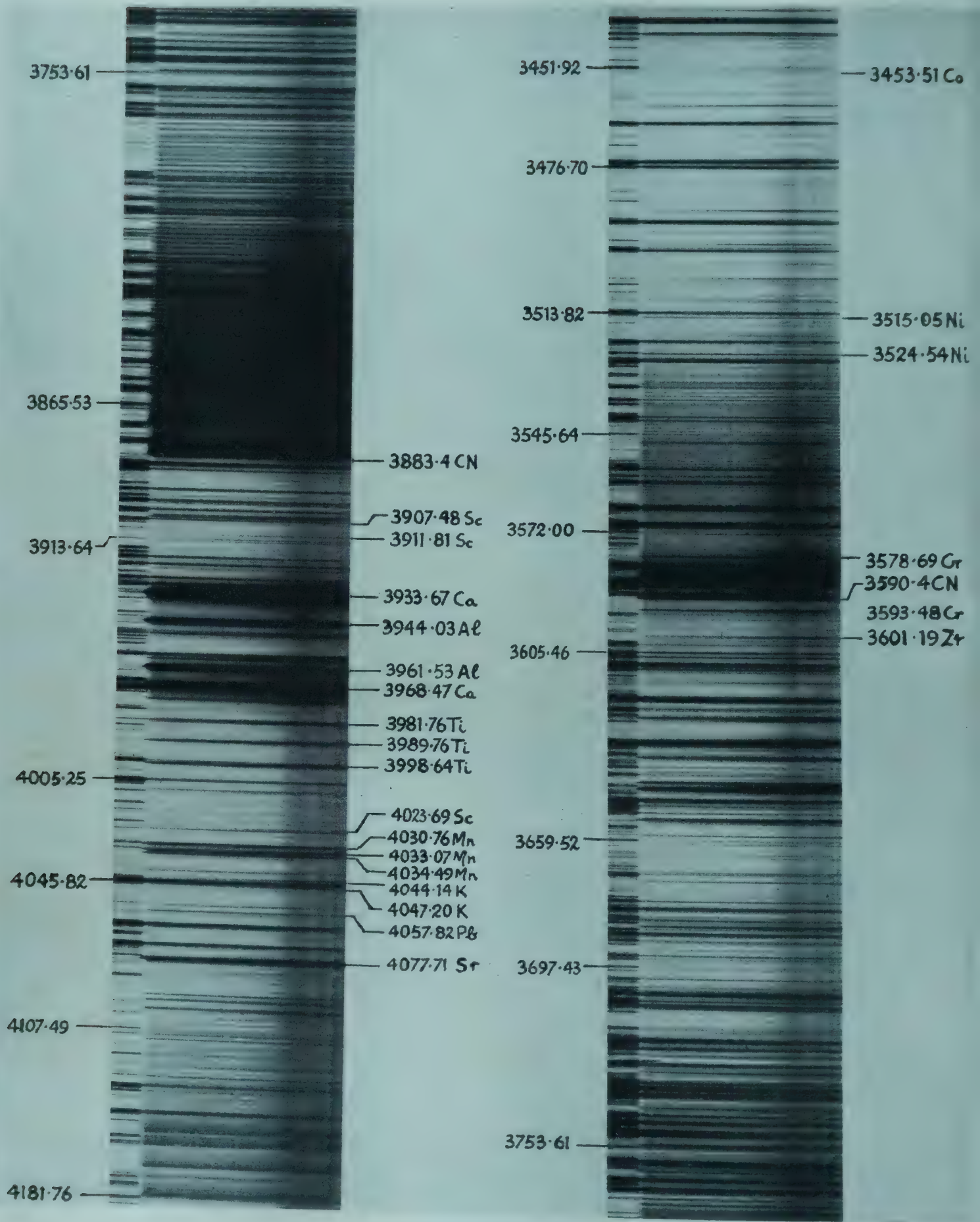
δ	0	1	2	3	4	5	6	7	8	9
0·56	0·420	0·421	0·423	0·424	0·426	0·427	0·428	0·430	0·431	0·432
0·57	0·434	0·435	0·437	0·438	0·439	0·441	0·442	0·443	0·445	0·446
0·58	0·447	0·449	0·450	0·452	0·453	0·454	0·456	0·457	0·458	0·460
0·59	0·461	0·462	0·464	0·465	0·466	0·468	0·469	0·470	0·472	0·473
0·60	0·474	0·476	0·477	0·478	0·480	0·481	0·482	0·484	0·485	0·486
0·61	0·488	0·489	0·490	0·492	0·493	0·494	0·496	0·497	0·498	0·500
0·62	0·501	0·502	0·504	0·505	0·506	0·507	0·509	0·510	0·511	0·513
0·63	0·514	0·515	0·517	0·518	0·519	0·521	0·522	0·523	0·524	0·526
0·64	0·527	0·528	0·530	0·531	0·532	0·533	0·535	0·536	0·537	0·539
0·65	0·540	0·541	0·543	0·544	0·545	0·546	0·548	0·549	0·550	0·551
0·66	0·553	0·554	0·555	0·557	0·558	0·559	0·560	0·562	0·563	0·564
0·67	0·566	0·567	0·568	0·569	0·571	0·572	0·573	0·574	0·576	0·577
0·68	0·578	0·579	0·581	0·582	0·583	0·585	0·586	0·587	0·588	0·590
0·69	0·591	0·592	0·593	0·595	0·596	0·597	0·598	0·600	0·601	0·602
0·70	0·603	0·605	0·606	0·607	0·608	0·610	0·611	0·612	0·613	0·615
0·71	0·616	0·617	0·618	0·620	0·621	0·622	0·623	0·624	0·626	0·627
0·72	0·628	0·629	0·631	0·632	0·633	0·634	0·636	0·637	0·638	0·639
0·73	0·641	0·642	0·643	0·644	0·645	0·647	0·648	0·649	0·650	0·652
0·74	0·653	0·654	0·655	0·656	0·658	0·659	0·660	0·661	0·663	0·664
0·75	0·665	0·666	0·667	0·669	0·670	0·671	0·672	0·673	0·675	0·676
0·76	0·677	0·678	0·680	0·681	0·682	0·683	0·684	0·686	0·687	0·688
0·77	0·689	0·690	0·692	0·693	0·694	0·695	0·696	0·698	0·699	0·700
0·78	0·701	0·702	0·704	0·705	0·706	0·707	0·708	0·710	0·711	0·712
0·79	0·713	0·714	0·716	0·717	0·718	0·719	0·720	0·721	0·723	0·724
0·80	0·725	0·726	0·727	0·729	0·730	0·731	0·732	0·733	0·735	0·736
0·81	0·737	0·738	0·739	0·740	0·742	0·743	0·744	0·745	0·746	0·748
0·82	0·749	0·750	0·751	0·752	0·753	0·755	0·756	0·757	0·758	0·759
0·83	0·760	0·762	0·763	0·764	0·765	0·766	0·768	0·769	0·770	0·771
0·84	0·772	0·773	0·775	0·776	0·777	0·778	0·779	0·780	0·782	0·783
0·85	0·784	0·785	0·786	0·787	0·789	0·790	0·791	0·792	0·793	0·794
0·86	0·795	0·797	0·798	0·799	0·800	0·801	0·802	0·804	0·805	0·806
0·87	0·807	0·808	0·809	0·811	0·812	0·813	0·814	0·815	0·816	0·817
0·88	0·819	0·820	0·821	0·822	0·823	0·824	0·826	0·827	0·828	0·829
0·89	0·830	0·831	0·832	0·834	0·835	0·836	0·837	0·838	0·839	0·840
0·90	0·842	0·843	0·844	0·845	0·846	0·847	0·848	0·850	0·851	0·852
0·91	0·853	0·854	0·855	0·856	0·858	0·859	0·860	0·861	0·862	0·863
0·92	0·864	0·866	0·867	0·868	0·869	0·870	0·871	0·872	0·873	0·875
0·93	0·876	0·877	0·878	0·879	0·880	0·881	0·883	0·884	0·885	0·886
0·94	0·887	0·888	0·889	0·890	0·892	0·893	0·894	0·895	0·896	0·897
0·95	0·898	0·899	0·901	0·902	0·903	0·904	0·905	0·906	0·907	0·908
0·96	0·910	0·911	0·912	0·913	0·914	0·915	0·916	0·917	0·919	0·920
0·97	0·921	0·922	0·923	0·924	0·925	0·926	0·927	0·929	0·930	0·931
0·98	0·932	0·933	0·934	0·935	0·936	0·938	0·939	0·940	0·941	0·942
0·99	0·943	0·944	0·945	0·946	0·948	0·949	0·950	0·951	0·952	0·953
1·00	0·954	0·955	0·956	0·958	0·959	0·960	0·961	0·962	0·963	0·964
1·0	0·954	0·965	0·976	0·987	0·998	1·009	1·020	1·031	1·042	1·053
1·1	1·064	1·075	1·086	1·097	1·107	1·118	1·129	1·140	1·151	1·161
1·2	1·172	1·182	1·193	1·204	1·214	1·225	1·236	1·246	1·257	1·267
1·3	1·278	1·288	1·299	1·309	1·320	1·330	1·341	1·351	1·362	1·372
1·4	1·382	1·393	1·403	1·414	1·424	1·434	1·445	1·455	1·465	1·476
1·5	1·486	1·496	1·507	1·517	1·527	1·538	1·548	1·558	1·568	1·579
1·6	1·589	1·599	1·609	1·620	1·630	1·640	1·650	1·661	1·671	1·681
1·7	1·691	1·701	1·712	1·722	1·732	1·742	1·752	1·763	1·773	1·783
1·8	1·793	1·803	1·813	1·824	1·834	1·844	1·854	1·864	1·874	1·884
1·9	1·895	1·905	1·915	1·925	1·935	1·945	1·955	1·965	1·975	1·986
2·0	1·996	2·006	2·016	2·026	2·036	2·046	2·056	2·066	2·076	2·086
2·1	2·097	2·107	2·117	2·127	2·137	2·147	2·157	2·167	2·177	2·187
2·2	2·197	2·207	2·217	2·227	2·237	2·248	2·258	2·268	2·278	2·288
2·3	2·298	2·308	2·318	2·328	2·338	2·348	2·358	2·368	2·378	2·388
2·4	2·398	2·408	2·418	2·428	2·438	2·448	2·458	2·469	2·479	2·489
2·5	2·499	2·509	2·519	2·529	2·539	2·549	2·559	2·569	2·579	2·589

APPENDIX III

Cathode layer arc spectrogram, from 8100 to 2480A of a material consisting mainly of SiO_2, Al_2O_3, Fe_2O_3, alkalis and alkaline earths, with the more important trace-constituent lines indicated, and with a comparison iron spectrum. Taken on a Hilger E1 Large Quartz Spectrograph.


5615·65
5857·46 Ca
5889·95 Na
5895·92 Na
6136·62
6137·70
6230·73
6494·99
6707·84 Li
6717·69 Ca
7664·91 K
7698·98 K
7800·23 Rb
7947·60 Rb
8079·02 Cs


4736·78
4871·33
4890·77
4920·51
4934·09 Ba
4957·61
4981·73 Ti
4991·07 Ti
4999·51 Ti
5007·21 Ti
5051·64
5167·49
5232·94
5264·24 Ca
5265·56 Ca
5270·28 Ca
Band CaF_2
5397·13
5455·61
5535·55 Ba
5615·65
4181·76
4216·0 CN
4226·73 Ca
4246·83 Sc
4250·79
4254·35 Cr
4274·80 Cr
4315·09
4379·24 V
4383·55
4425·44 Ca
4427·31
4434·96 Ca
4435·69 Ca
4442·34
4454·78 Ca
4455·89 Ca
4511·32 In
4528·62
4554·04 Ba
4578·56 Ca
4581·40 Ca
4585·87 Ca
4602·86 Li
4602·94
4607·33 Sr
4736·78


3753·61
3865·53
3913·64
4005·25
4045·82
4107·49
4181·76
3883·4 CN
3907·48 Sc
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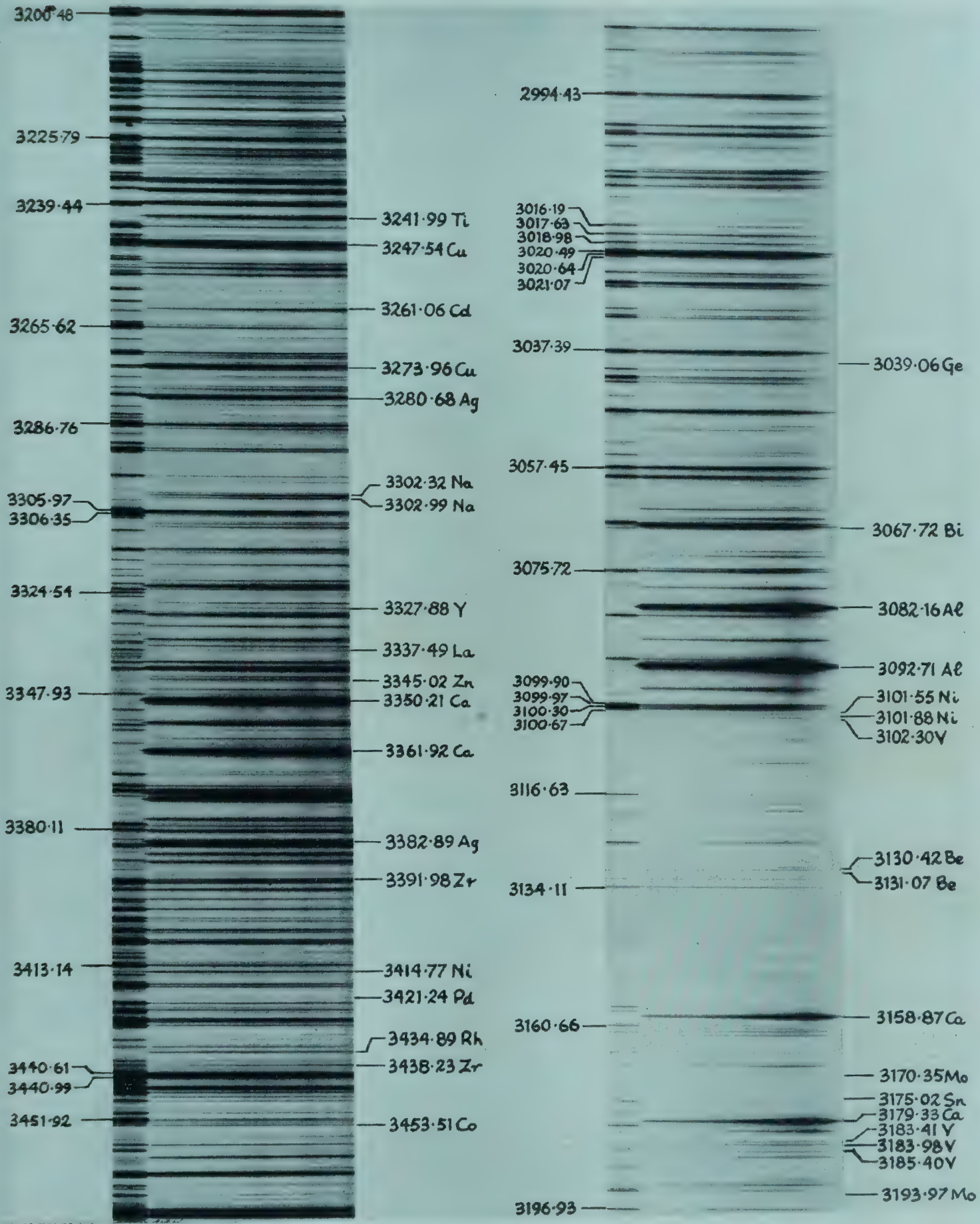
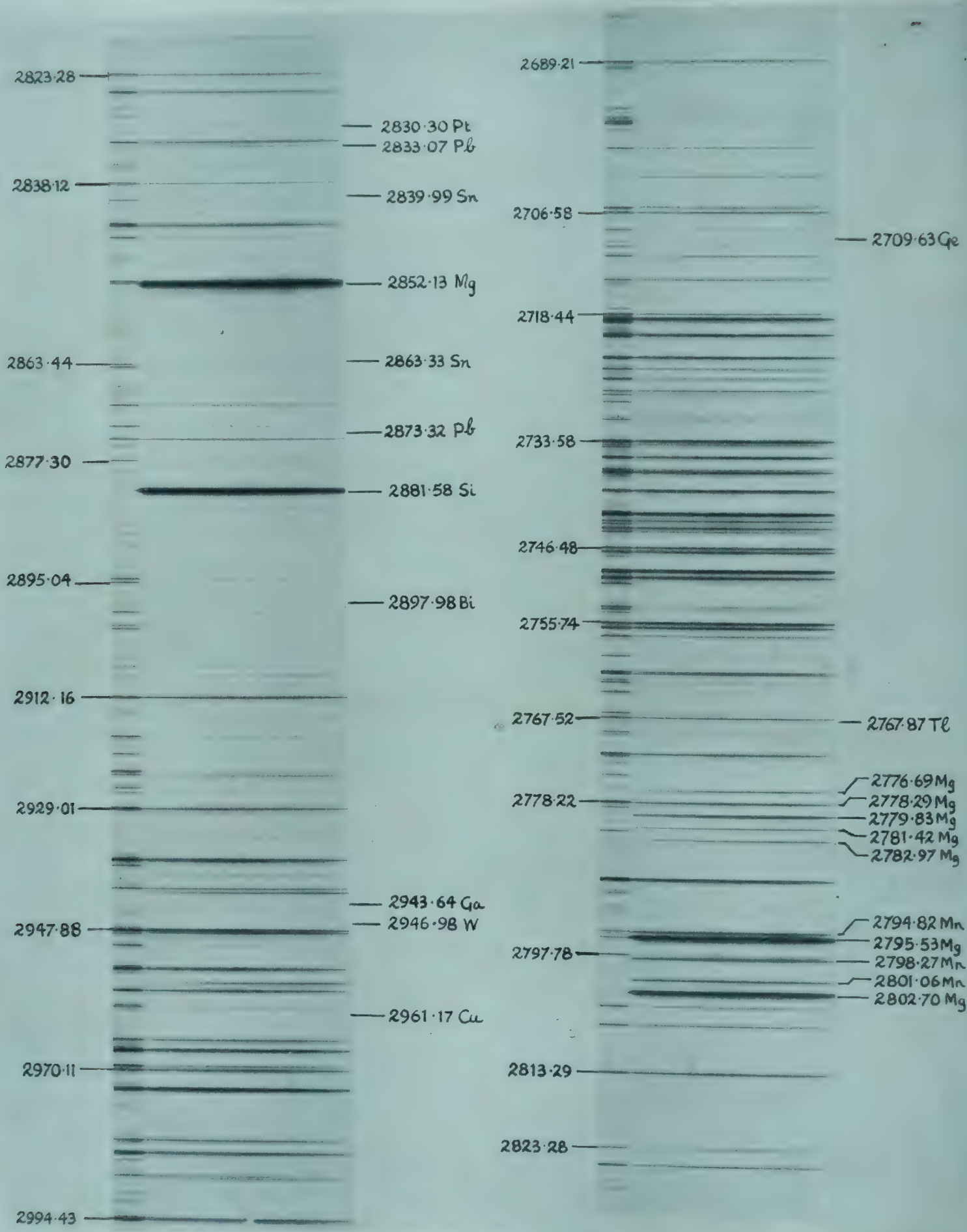
3933·67 Ca
3944·03 Al
3961·53 Al
3968·47 Ca
3981·76 Ti
3989·76 Ti
3998·64 Ti
4023·69 Sc
4030·76 Mn
4033·07 Mn
4034·49 Mn
4044·14 K
4047·20 K
4057·82 Pb
4077·71 Sr
3451·92
3476·70
3513·82
3545·64
3572·00
3605·46
3659·52
3697·43
3753·61
3453·51 Co
3515·05 Ni
3524·54 Ni
3578·69 Cr
3590·4 CN
3593·48 Cr
3601·19 Zr


3200·48
3225·79
3239·44
3241·99 Ti
3247·54 Cu
3261·06 Cd
3265·62
3273·96 Cu
3280·68 Ag
3286·76
3302·32 Na
3305·97
3302·99 Na
3306·35
3324·54
3327·88 Y
3337·49 La
3345·02 Zn
3347·93
3350·21 Ca
3361·92 Ca
3380·11
3382·89 Ag
3391·98 Zr
3413·14
3414·77 Ni
3421·24 Pd
3434·89 Rh
3440·61
3438·23 Zr
3440·99
3451·92
3453·51 Co
2994·43
3016·19
3017·63
3018·98
3020·49
3020·64
3021·07
3037·39
3039·06 Ge
3057·45
3067·72 Bi
3075·72
3082·16 Al
3092·71 Al
3099·90
3099·97
3100·30
3100·67
3101·55 Ni
3101·88 Ni
3102·30 V
3116·63
3130·42 Be
3131·07 Be
3134·11
3158·87 Ca
3160·66
3170·35 Mo
3175·02 Sn
3179·33 Ca
3183·41 V
3183·98 V
3185·40 V
3193·97 Mo
3196·93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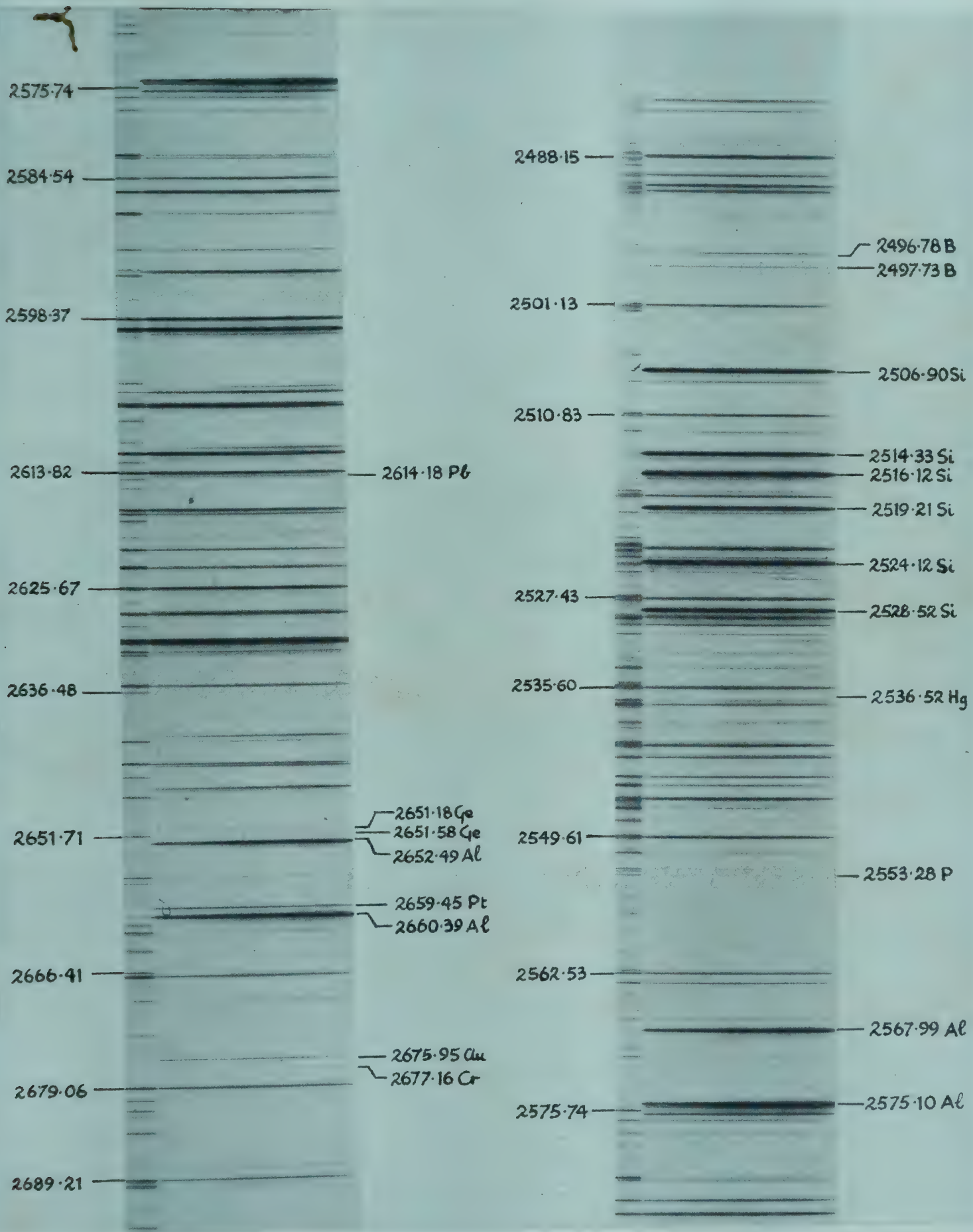
2833·07 Pb
2838·12
2839·99 Sn
2852·13 Mg
2863·44
2863·33 Sn
2873·32 Pb
2877·30
2881·58 Si
2895·04
2897·98 Bi
2912·16
2929·01
2943·64 Ga
2947·88
2946·98 W
2961·17 Cu
2970·11
2994·43
2689·21
2706·58
2709·63 Ge
2718·44
2733·58
2746·48
2755·74
2767·52
2767·87 Tl
2776·69 Mg
2778·22
2778·29 Mg
2779·83 Mg
2781·42 Mg
2782·97 Mg
2794·82 Mn
2795·53 Mg
2797·78
2798·27 Mn
2801·06 Mn
2802·70 Mg
2813·29
2823·28


2575·74
2584·54
2598·37
2613·82
2614·18 Pb
2625·67
2636·48
2651·71
2651·18 Ge
2651·58 Ge
2652·49 Al
2659·45 Pt
2660·39 Al
2666·41
2675·95 Au
2677·16 Cr
2679·06
2689·21
2488·15
2496·78 B
2497·73 B
2501·13
2506·90 Si
2510·83
2514·33 Si
2516·12 Si
2519·21 Si
2524·12 Si
2527·43
2528·52 Si
2535·60
2536·52 Hg
2549·61
2553·28 P
2562·53
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2575·74
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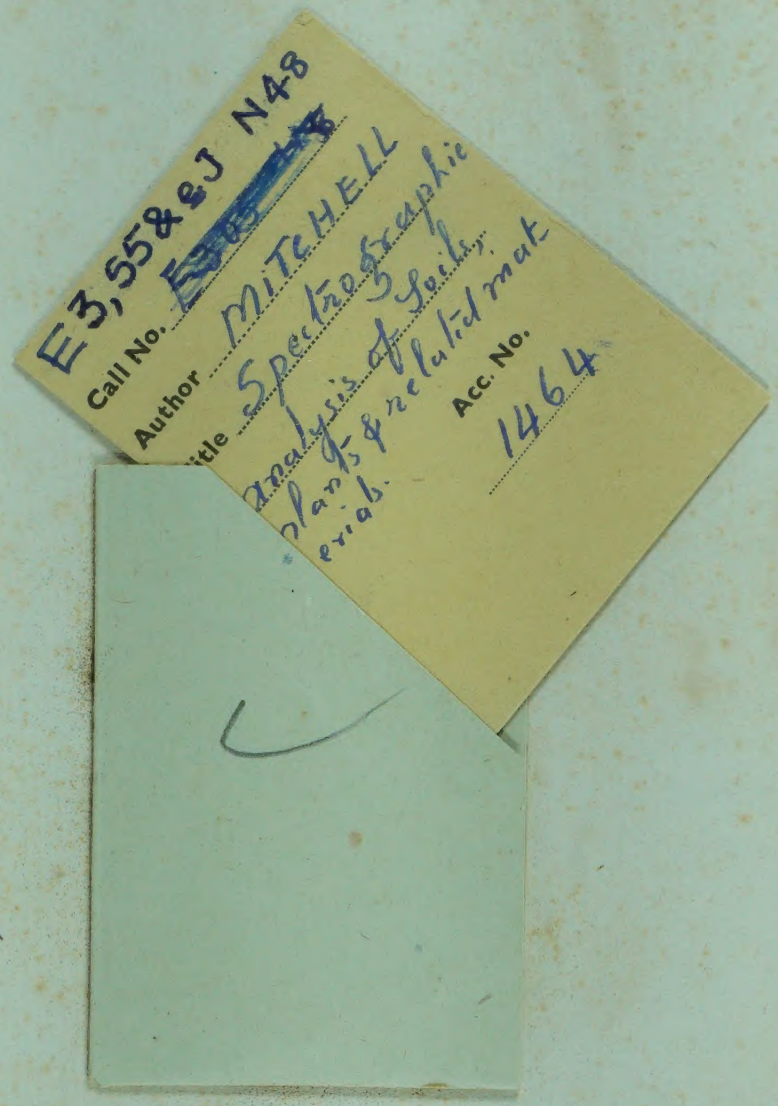
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